Phonon lifetimes from first-principles self-consistent lattice dynamics

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Abstract
Phonon lifetime calculations from first principles usually rely on time-consuming molecular dynamics calculations, or density functional perturbation theory where the zero-temperature crystal structure is assumed to be dynamically stable. Here is presented a new and effective method for calculating phonon lifetimes from first principles. This method is not limited to crystallographic phases stable at 0 K and provides a scheme more effective than most corresponding molecular dynamics calculations. The method is based on the recently developed self-consistent ab initio lattice dynamical method and is here tested by calculating the bcc phase phonon lifetimes of Li, Na, Ti and Zr as representative examples.

1. Introduction
Calculations of phonon lifetimes are of great interest to the materials science community, partly in that they allow the prediction of thermal transport properties, which in themselves are important from an engineering perspective, but also since these properties are closely interrelated to perhaps the even more intriguing thermoelectric effect [1].

Phonon lifetime calculations from first principles have been performed for quite some time, for instance see the work of Katsnelson et al [2] or Debernardi et al [3]. More recently Koker [4] successfully calculated the thermal transport coefficients for MgO within the context of ab initio molecular dynamics (ab-MD) [5] and Bonini et al [6] estimated the optical phonon linewidths in graphene using density functional perturbation theory (DFPT) [7–9].

Up to the present date ab-MD and DFPT have been the two main methods of choice used for calculating phonon lifetimes from first principles. However, the use of ab-MD suffers from the long simulation times required to sample the correlation functions, whereas DFPT is limited to crystal structures stable at zero temperature, in that it only calculates third-order anharmonic contributions. Thus, there is still a need for more effective methods, preferably based upon schemes that also allow lifetime calculations in crystallographic phases stabilized only at finite temperatures, such as the bcc phase of Ti, Zr and Hf and the cubic phases of numerous shape memory alloys.

In this paper a novel and effective method for calculating phonon lifetimes, which do not suffer from the limitations of ab-MD and DFPT, will be presented. The method is based on the recently developed self-consistent ab initio lattice dynamical scheme (SCAILD) [10], which has previously been successfully used in predicting phonon frequency renormalization by strong anharmonicity [11, 12]. The newly developed method will be used here to calculate phonon lifetimes in the bcc phase of Li, Na, Ti and Zr in order to illustrate its effectiveness.

2. Method
The SCAILD method is based on the calculation of Hellman–Feynman forces of atoms in a supercell. The method can be viewed as an extension of the frozen phonon method [13], in which all phonons with wavevectors \( \mathbf{q} \) commensurate with the supercell are excited together in the same cell by displacing atoms situated at the undistorted positions \( \mathbf{R} + \mathbf{b}_\sigma \), according to \( \mathbf{R} + \mathbf{b}_\sigma \rightarrow \mathbf{R} + \mathbf{b}_\sigma + \mathbf{U}(\mathbf{R}) \), where the displacements are given by

\[
\mathbf{U}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}, \sigma} A_{\mathbf{q}, \sigma}^R e^{i \mathbf{q} \cdot \mathbf{R}} e^{i \mathbf{q} \cdot \mathbf{b}_\sigma}.
\]

(1)
Here $\mathbf{R}$ represent the $N$ Bravais lattice sites of the supercell, $b_\sigma$ the position of atom $\sigma$ relative to the lattice site, $\epsilon_{qs}^\sigma$ are the phonon eigenvectors corresponding to the phonon mode, $s$, and the mode amplitude $A^\sigma_q$ is calculated from the different phonon frequencies $\omega_{qs}$ through

$$A^\sigma_q = \pm \sqrt{ \frac{h}{M^\sigma_0 \omega_{qs}^2} \left( \frac{1}{2} + n_{qs}^\sigma \right) },$$

where $n_{qs}^\sigma = n(\epsilon_{qs}^\sigma)$, with $n(x) = 1/(e^x - 1)$, are the phonon occupational numbers, $M^\sigma_0$ the atomic masses and $T$ is the temperature of the system. The phonon frequencies, $\omega_{qs}$, are obtained through the projections of the Fourier transformed atomic forces, $F^\sigma_{qs}$, onto the eigenvectors of the corresponding mode:

$$\omega_{qs}^2 = - \sum_\sigma \frac{\epsilon_{qs}^\sigma \cdot F^\sigma_{qs}}{A^\sigma_q M^\sigma_0}.$$  

Before we continue, we note in passing that it is through the Bose–Einstein occupational factors, $n_{qs}$, appearing in the amplitudes $A^\sigma_q$, that the temperature dependence is introduced to the renormalized phonon frequencies and lifetimes.

Due to the simultaneous presence of all the commensurate phonons in the same force calculation, the interaction between different lattice vibrations is taken into account and the phonon frequencies given by equation (3) are thus renormalized by the very same interaction.

By alternating between calculating the forces on the displaced atoms and calculating new phonon frequencies and new displacements through equations (1)–(3) the phonon displaced atoms and calculating new phonon frequencies and renormalized by the very same interaction.

At each SCAILD iteration, here indexed $i$, a set of $m_q$ symmetry-equivalent frequencies $\omega_{qs}(i,j)$, for every commensurate phonon mode [14, 15]. Throughout the $N_I$ SCAILD iterations these sets are used to accumulate sample sets, $\omega_{qs}(i,j)_{i=1,...,N_I}$, from which frequency distributions,

$$D(\omega_{qs}^\sigma) = \frac{1}{N} \sum_{i=1}^{N_I} \sum_{j=1}^{m_q} e^{-[\omega_{qs}^\sigma - \omega_{qs}(i,j)]^2 / g^2},$$

are generated. Here $g$ is a Gaussian smearing parameter and $N$ is a normalization constant chosen such that $\int D(\omega_{qs}^\sigma) d\omega_{qs}^\sigma = 1$. By calculating the first moment, $\Omega_{qs}^2$, of these distributions the renormalized phonon frequencies are obtained [10].

The novel implementation of the SCAILD scheme utilizes the possibility of extracting the phonon lifetimes from the frequency distributions, $D(\omega_{qs}^\sigma)$. To establish the connection between the phonon lifetime, $\tau_{qs}$, of a mode and its corresponding distribution $D(\omega_{qs}^\sigma)$, we start from the Newtonian equations of motion of a stochastically damped phonon mode:

$$\frac{d^2 A^\sigma_q}{dt^2} = -\Gamma_{qs} A^\sigma_q - \Omega_{qs}^2 A^\sigma_q + a(t),$$

where $\Gamma_{qs} = 1/\tau_{qs}$ is the phonon linewidth (damping) and $a(t)$ is the stochastic acceleration arising from the interaction between the mode and the other phonons of the system. The replacement of interaction terms by stochastic variables is, in path-integral approaches, associated with the Stratonovich–Hubbard transformation [16], and in more classical contexts associated with discussions concerning the fluctuation–dissipation theorem [17].

Following a path similar to what is generally used in proving the fluctuation–dissipation theorem [17, 18], the damping $\Gamma_{qs}$ is formally connected to the acceleration correlation function, $C(t) \equiv \langle a(t) a(t + \tau) \rangle$, through the integral equation

$$\Gamma_{qs} = \frac{2M^\sigma_0}{3k_B T} \frac{\Omega_{qs}}{2M^\sigma_0 v_{qs}}^2 C^s(\Gamma_{qs}),$$

where the brackets $\langle \cdot \rangle$ denote an ensemble average, $v_{qs} = \Omega_{qs}^2 - (\Gamma_{qs}/2)^2$ and $C^s$ is given by

$$C^s(\Gamma_{qs}) = \int_{-\infty}^\infty d\nu [\cos(v_{qs} \nu) - \alpha_{qs} \cos(v_{qs} |\nu| + \delta_{qs})] \times C(\nu) e^{-\Gamma_{qs} |\nu|}.$$  

Here $\tan(\delta_{qs}) = 2v_{qs}/\Gamma_{qs}$ and $\alpha_{qs} = (\Gamma_{qs}/2)\Omega_{qs}^{-1}$.

Even though equations (6) and (7), in principle provide a connection between the stochastic friction forces and the phonon lifetimes, we will here instead follow an alternative approach in order to extract the phonon lifetimes, which is more convenient when employed in the context of the SCAILD scheme.

The phonon frequencies obtained through the SCAILD scheme, equation (3), can be related to the homogeneous (transient) solutions to equation (5), i.e. solutions achieved with $a(t) = 0$, through the definition

$$\omega_{qs}^2 \equiv -\frac{1}{A_{qs}^\sigma} \frac{d^2 A_{qs}^\sigma}{dt^2} = \frac{\Gamma_{qs}}{A_{qs}^\sigma} \frac{dA_{qs}^\sigma}{dt} + \Omega_{qs}^2.$$  

By assuming that the temperature is high enough for a classical description to be valid, we can use the transient solutions of equation (5) together with equation (8) to obtain the following relation:

$$D(\omega_{qs}^\sigma) \sim \left( \frac{d\omega_{qs}^\sigma}{dt} \right)^{-1} = \frac{\Gamma_{qs}}{(\Gamma_{qs}^2 v_{qs})^2 + (\omega_{qs}^2 - \Omega_{qs}^2)^2}. $$

between the frequency distributions and the phonon lifetimes. Thus it becomes evident that the distribution equation (9) calculated within the SCAILD scheme corresponds, within a multiplicative constant, to the dynamical structure factor of a stochastically damped harmonic oscillator in the high temperature classical limit [19, 20].

Another important observation to make at this point is that the frequency distributions can be obtained despite the absence of any explicit time dependence in the SCAILD scheme, by virtue of the stochastic damping and the ergodic principle. This is realized by choosing the magnitude of the frozen phonon amplitudes $A_{qs}^\sigma$ such that they reproduce the atomic mean square displacements dictated by thermodynamics, and by the re-randomization of the
Figure 1. Calculated phonon lifetimes (full black circles) for (a) bcc-Li and (b) bcc-Na, displayed together with experimental data (red squares) [22–24]. The full lines connect lifetimes corresponding to longitudinal modes, the dashed lines connect lifetimes corresponding to the transverse $T_1$ modes and the dotted lines connect lifetimes corresponding to the transverse $T_2$ modes. The calculations were performed at a temperature of 293 K, whereas the experimental data for bcc-Li and bcc-Na were obtained at 293 K and 296 K, respectively.

frozen phonon phases at each new SCAILD iteration, here represented by the randomization of the $\pm$ signs of the amplitudes $A_{q^s}^\sigma$ (see equation (2)).

It is also of importance to make clear that it is only the mean frequencies $\Omega_{q^s}^2$, and not the entire frequency distributions $D(\omega_{q^s}^2)$, that are used in order to calculate the phonon density of states\(^1\), and the associated integrated properties such as the internal and free energy. Consequently, the lattice dynamical free energy converges much faster than properties extracted from the full phonon distributions. Hence the $\sim$40 iterations reported to be enough for reaching a free energy convergence of $\sim$1 meV between consecutive SCAILD iterations [14] was far from enough to estimate the phonon lifetimes. Therefore, the phonon frequency distributions had to be obtained through $N_I = 200$ SCAILD iterations together with a Gaussian smearing, $g = 0.05$ THz\(^2\), applied to each of the sampled squared frequencies. The applied smearing, $g$, was well below the widths of the calculated distributions $D(\omega_{q^s}^2)$.

Regarding the other computational details of the force calculation the VASP package [21] was used, within the generalized gradient approximation (GGA). The projector augmented wave (PAW) potentials required energy cutoffs of 210 eV, 125 eV, 200 eV and 170 eV for Li, Na, Ti and Zr, respectively. The $k$-point mesh used was a $3 \times 3 \times 3$ Monkhorst–Pack mesh. Since the Methfessel–Paxton smearing of 0.2 eV, generally prescribed to obtain accurate interatomic forces, corresponds to an electronic temperature of $\sim$2300 K which is much higher than the temperatures at which the phonon lifetimes were to be calculated, the use of Fermi–Dirac smearing of the electronic subsystem was abandoned and the 0.2 eV Methfessel–Paxton smearing was employed throughout all the calculations. To evaluate how the choice of Methfessel–Paxton smearing over Fermi–Dirac smearing affects the calculated phonon lifetimes, additional calculations on bcc-Li were performed using Fermi–Dirac smearing together with an electronic temperature of 293 K. The phonon lifetimes calculated with the two different smearing schemes differed by $\lesssim 0.1$ THz.

The supercells used were obtained by increasing the bcc primitive cells eight times along the primitive lattice vectors, resulting in 512-atom cells. In order to evaluate the finite size effects, a smaller 64-atom supercell was also used to calculate the phonon lifetimes in bcc-Ti. The differences between phonon lifetimes obtained in the 64-atom cell and the 512-atom cell were $\sim 0.1$ THz.

3. Results

In figures 2 and 4 the calculated frequency distributions of bcc-Li, bcc-Na, bcc-Ti and bcc-Zr are presented together with their respective fits to equation (9). Here the distributions obtained from the SCAILD iterations are found to be in excellent agreement with the fits to equation (9). Furthermore, in figures 1 and 3 the phonon lifetimes extracted from the fits to equation (9) are displayed together with experimental data. Here good agreement between theory and experiment can be found in the [110] direction for bcc-Na, bcc-Ti and

\(^1\) In practice, the phonon density of states is obtained through Fourier interpolation of the frequencies, $\Omega_{q^s}^2$, on a $q$-point mesh that is much more dense than the commensurate mesh.
Figure 2. The calculated $T_1$ mode frequency distribution for bcc-Li and bcc-Na along the $[\xi \xi 0]$ direction, for $\xi = 0.125, 0.250, 0.375$ and 0.500 (dashed black lines). The full red curves were obtained through the fitting of the data with equation (9). The calculations were performed at the finite temperature of 293 K.

bcc-Zr, whereas a potentially quite huge discrepancy can be found for bcc-Zr in the [112] direction at $\xi = 0.35$. This discrepancy is referred to as potential due to the fact that the experimental $q$-point corresponding to $\xi = 0.35$ does not belong to the $q$-point set used in the calculation and because linear interpolation between lifetimes corresponding to different $q$-points is not always a good approximation to employ. Finally, it can also be observed that the theoretical phonon lifetimes in the case of bcc-Li are well within the experimental error bars.

3.1. The contribution of the electron–phonon coupling to the lifetimes

In this work the only anharmonic contributions to the phonon lifetimes have been taken into account, completely excluding any electron–phonon coupling (ep) effects. The
Figure 3. Calculated phonon lifetimes (full black circles) for (a) bcc-Ti and (b) bcc-Zr, displayed together with experimental data (red squares, blue diamonds and green triangles) [25, 26]. The full lines connect lifetimes corresponding to longitudinal modes, the dashed lines connect lifetimes corresponding to the transverse $T_1$ modes and the dotted lines connect lifetimes corresponding to the transverse $T_2$ modes. The calculations were performed at a temperature of 1300 K, whereas the temperature for which the experimental data were obtained is given in the figure. All the experimental lifetimes correspond to transverse $T_1$ modes.

electron–phonon-related contribution to the phonon lifetime, in the cases of bcc-Li and bcc-Na, has been calculated from first principles by Liu et al. [27], reporting values of $1/\tau_{\text{ep}}^{\text{Li}} \lesssim 3 \times 10^{-2}$ THz and $1/\tau_{\text{ep}}^{\text{Na}} \lesssim 8 \times 10^{-3}$ THz.

In the case of bcc-Ti and bcc-Zr, probably due to the dynamical instability of the bcc phase at low temperatures, no available data on the electron–phonon contribution to the phonon lifetimes have been found. However, the electron–phonon coupling constant, $\lambda$, for bcc-Ti and bcc-Zr can be estimated from the McMillan–Hopfield parameter, $\eta$, through the relation

$$\lambda = \frac{\eta}{M\bar{\omega}^3}. \quad (10)$$

Here $M$ is the mass of the atom and $\bar{\omega}$ the mean phonon frequency. Sigalas et al. [28] have calculated the McMillan–Hopfield parameter to $\eta_{\text{bcc-Ti}} = 6.3085$ eV Å$^{-2}$ and $\eta_{\text{bcc-Zr}} = 5.6925$ eV Å$^{-2}$. Furthermore, by assuming an equal lifetime, $1/\tau_{\text{ep}}$, for all phonon modes and approximating the phonon density of states with a Debye spectrum, the Eliashberg function $\alpha^2 F(\omega)$ [29] can be approximated to

$$\alpha^2 F(\omega) = \frac{1}{2\pi N_F} \sum_{q,s} \frac{(\tau_{\text{ep}}^s)^{-1}}{\omega_q^s} \times \delta(\omega - \omega_q^s) \approx \frac{3}{2\pi N_F} \frac{\omega}{\hbar \omega_D^3}, \quad (11)$$

where $N_F$ is the electron density of states at the Fermi level and $\omega_D$ the Debye frequency. From the above approximation of the Eliashberg function, an alternative expression for the electron–phonon coupling constant can be estimated:

$$\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega = \frac{6}{2\pi N_F} \frac{1}{\hbar \omega_D^2}. \quad (12)$$

By assuming that $\bar{\omega} \approx \omega_D$, combining equation (10) with equation (12) and solving for $1/\tau_{\text{ep}}$, we finally get an estimate for the electron–phonon-related lifetime:

$$\frac{1}{\tau_{\text{ep}}} = \frac{2}{6M} \frac{2\pi \eta N_F \hbar}{\omega_{\text{ep}}} \approx \frac{1}{\tau_{\text{ep}}} \approx 0.1 \text{ THz and } 1/\tau_{\text{ep}} \approx 0.05 \text{ THz.} \quad (13)$$

From the above considerations it becomes clear that the anharmonic contribution to the phonon lifetimes in the bcc phase of Li, Na, Ti and Zr is at least one order of magnitude larger than the lifetimes emanating from the electron–phonon interaction.

4. Conclusion

In summary, a novel, effective and simple method for calculating phonon lifetimes has been presented together with some test calculations on the bcc phase occurring at room
Figure 4. The calculated $T_1$ mode frequency distribution for bcc-Ti and bcc-Zr along the $[\xi\xi0]$ direction, for $\xi = 0.125, 0.250, 0.375$ and $0.500$ (dashed black lines). The full red curves were obtained through the fitting of the data with equation (9). The calculations were performed at the finite temperature of 1300 K.

temperature as well as for temperatures well above 1000 K, for Li, Na, Ti and Zr. The method has provided good estimates for most of the phonon lifetimes, and shows promise as an effective tool in calculating phonon linewidths, especially for crystal structures that can only be stabilized at elevated temperatures, thus opening the door to phonon lifetime calculations from first principles in cases when anharmonic interactions of order $\geq 3$ are important for achieving a correct description of the system under study.

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