Abstract

We here introduce a Fortran code that computes anharmonic free energy of solids from first-principles based on our phonon quasiparticle approach. In this code, phonon quasiparticle properties, i.e., renormalized phonon frequencies and lifetimes, are extracted from mode-projected velocity auto-correlation functions (VAF) of modes sampled by molecular dynamics (MD) trajectories. Using renormalized frequencies as input, the code next constructs an effective harmonic force constant matrix to calculate anharmonic phonon dispersions over the whole Brillouin zone and thus the anharmonic free energy in the thermodynamic limit ($N \to \infty$). We illustrate the use of this code to compute \textit{ab initio} temperature-dependent anharmonic phonons of Si in the diamond structure.

Keywords: Velocity auto-correlation function; Anharmonic phonon dispersion; Phonon quasiparticle; First-principles molecular dynamics; Lattice dynamics

PROGRAM SUMMARY

Program title: \textit{phq}

Licensing provisions: GPLv3

Programming language: Fortran 90

Operating system: Linux, macOS, Windows

Nature of problem:
Accurate free energy calculations deliver predictive thermodynamic properties of solids. Although the quasi-harmonic approximation (QHA) has been widely used for various materials, its validity at very high temperatures is not guaranteed because of intrinsic anharmonic effects. The QHA cannot be used even at low temperatures for strongly anharmonic systems, e.g., those that are stabilized by anharmonic fluctuations. When anharmonicity is non-negligible, phonon frequencies display a pronounced dependence on temperature, which impacts thermodynamic properties. Therefore, the calculation of anharmonic phonon dispersions is critical for an accurate estimation of the free energy.

Solution method:
We calculate phonon quasiparticle properties, i.e., renormalized phonon frequencies and lifetimes, by combing molecular dynamics (MD) trajectories and harmonic normal modes (HNM). MD velocities are

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projected into HNMs and the mode-projected velocity auto-correlation functions (VAF) are then calculated. Quasiparticle properties are then obtained by analyzing the VAFs, if they are well defined. Using the renormalized phonon frequencies and HNMs we build an effective (temperature-dependent) harmonic force constant matrix from which the anharmonic phonon dispersions can be obtained.

**Unusual features:**
(i) Because MD captures anharmonic effects to infinite order, this approach to compute renormalized phonon frequencies and lifetimes is expected to be more appropriate than lowest-order perturbation theory for strongly anharmonic systems or for weakly anharmonic systems at very high temperatures. (ii) By characterizing phonon quasiparticles, this approach provides a validity check of the phonon concept, a fundamental procedure missing in other approaches to compute anharmonic dispersions, e.g., the self-consistent phonon method.

1. Introduction

The phonon gas model (PGM) \([1, 2, 3, 4]\) provides an excellent paradigm for calculating thermodynamics properties of materials. For weakly anharmonic systems, anharmonic effects reflecting the intrinsic temperature dependence of phonon frequencies are negligible. Thus, the quasiharmonic approximation (QHA) \([5, 6]\) offers predictive free energies and thermodynamics properties. Note that the QHA accounts for the extrinsic temperature dependence of the phonon frequencies caused by volume changes (thermal expansion). However, in strongly anharmonic systems, intrinsic anharmonic effects are key to structural stabilization and must be properly accounted for. Therefore, anharmonic phonon dispersions are required for estimations of free energy and related thermodynamic properties.

Here we introduce a code of a hybrid approach which fully accounts for anharmonic effects. In this approach, we describe a phonon quasiparticle of normal mode \((q, s)\) by the mode-projected velocity autocorrelation functions (VAF) \([7]\),

\[
\langle V_{qs}(0) \cdot V_{qs}(t) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau V_{qs}^*(t')V_{qs}(t' + t)dt'.
\]

where,

\[
V_{qs}(t) = \sum_{i=1}^N V(t) \cdot e^{iq \cdot r_i} \cdot \hat{e}_{qs}
\]

is the \(s\)-th branch of \(q\)-projected velocity. \(\hat{e}_{qs}\) is the harmonic phonon polarization vector of mode \((q, s)\).

\[
V(t) = V(\sqrt{M_1}v_1(t), ..., \sqrt{M_N}v_N(t))
\]

is the weighted velocity with \(3N\) components. \(v_i(t)(i = 1, ..., N)\) are atomic velocities calculated from MD trajectories of an \(N\)-atom supercell. \(M_i\) is the atomic mass of the \(i^{th}\) atom in the supercell.

For a well-defined phonon quasiparticle, its power spectrum,

\[
G_{qs}(\omega) = \left| \int_0^\infty \langle V_{qs}(0) \cdot V_{qs}(t) \rangle e^{i\omega t} dt \right|^2.
\]

should have a Lorentzian line shape with a peak at \(\tilde{\omega}_{qs}\) and a linewidth of \(1/(2\tau_{qs})\), where \(\tau_{qs}\) is the lifetime of mode \((q, s)\) in the relaxation time approximation \([2, 3, 8]\). In principle, a complete
decay of \( \langle V_{qs}(0) \cdot V_{qs}(t) \rangle \) is required to obtain a reliable \( G_{qs} \). However, very long MD runs are needed to satisfy this condition for phonons with long lifetimes. This is inconvenient for \textit{ab initio} MD simulations. Here, we extract \( \tilde{\omega}_{qs} \) and \( \tau_{qs} \) from \( \langle V_{qs}(0) \cdot V_{qs}(t) \rangle \) phenomenologically from relatively shorter MD runs. For a well-defined phonon quasiparticle of mode \((q, s)\), one can simply fit \( \langle V_{qs}(0) \cdot V_{qs}(t) \rangle \) to the expression,

\[
A_{qs} \cos(\tilde{\omega}_{qs} t) e^{-t/(2\tau_{qs})}
\]

where, \( A_{qs} \) is the vibrational amplitude. In practice, to obtain reliable \( \tilde{\omega}_{qs} \) and \( \tau_{qs} \), the fitting needs only the numerical data of \( \langle V_{qs}(0) \cdot V_{qs}(t) \rangle \) for the first few oscillation periods.

With \( \tilde{\omega}_{qs} \) of those modes sampled by the MD run, an effective harmonic dynamical matrix can be constructed,

\[
\tilde{D}(q) = \hat{e}_q \Omega_q \hat{e}_q^\dagger,
\]

where,

\[
\Omega_q = \text{diag}[\tilde{\omega}_{q1}^2, \tilde{\omega}_{q2}^2, ..., \tilde{\omega}_{q3N}^2],
\]

and \( \hat{e}_q \) is the harmonic eigenvector matrix:

\[
\hat{e}_q = [\hat{e}_{q1}, \hat{e}_{q2}, ..., \hat{e}_{q3N}].
\]

The effective harmonic force constant matrix \( \tilde{\Phi}(r) \) can be obtained from the Fourier transformation of \( \tilde{D}(q) \), from which,

\[
\tilde{D}(q') = \sum_r \tilde{\Phi}(r) \cdot e^{-i q' \cdot r}
\]

the effective harmonic dynamical matrix at arbitrary wave vector \( q' \) is obtained. This way, \( \tilde{\omega}_{q' s} \) at any \( q' \) in the Brillouin zone are calculated by diagonalizing \( \tilde{D}(q') \).

This approach gives anharmonic phonon dispersions that are useful to study thermodynamic and lattice thermal transport properties of materials, especially at extreme conditions. It also offers a means of checking the existence of feasible vibrational modes even in the presence of strong anharmonicity. For example, we can witness the emergence of the cubic phase of \( \text{CaSiO}_3 \) perovskite at high temperature and high pressure [9]. The concept of phonon quasiparticle also helps to easily resolve mode frequencies in the vibrational spectrum that overlap in energy even in the presence of crystal structure complexity. This advantage has been demonstrated on \( \text{MgSiO}_3 \) perovskite, a typical non-trivial crystal structure with \textit{Pbnm} symmetry and 20 atoms/cell. The obtained subtle and irregular frequency shifts with temperature are in good agreement with experiments [10]. Recently, we applied this approach to beryllium metal to address phase transitions at temperatures near melting. Our calculations confirmed that the long-debated and controversial \textit{hcp} \( \rightarrow \text{bcc} \) transition occurs at very high temperatures, just before melting [11]. While the \textit{hcp} structure was shown to be dynamically stable at all temperatures up to the transition temperature, the \textit{bcc} phase was dynamically stabilized by anharmonic fluctuations just below the transition temperatures. At the phase boundary, both structures had phonon quasiparticles well defined and that was sufficient to enable free energy and phase boundary computations at those high temperatures. In addition, phonon lifetimes obtained this way allow us to study lattice thermal conductivity using the Boltzmann transport equation (BTE) approach. For instance, we demonstrated for the first time the breakdown of the well-known phonon minimal mean free theory in \( \text{MgSiO}_3 \) perovskite [12], a result later confirmed by lowest-order perturbation theory [13].

The procedure to compute quasiparticle properties consists of four key steps. Step 1, atomic velocities are calculated by carrying out MD simulations and recording velocities [Eq. (3)]. Step 2,
projecting instantaneous atomic velocities into the harmonic normal modes (HNM) [Eq. (2)]. Step 3, computing mode-projected velocity auto-correlation functions (VAF) and extracting quasiparticle frequencies and lifetimes from VAFs [Eq. (1)(4)(5)]. Step 4, constructing effective harmonic dynamical matrices using the renormalized phonon frequencies and HNMs and using them to obtain anharmonic phonon dispersions [Eq. (6)(7)(8)(9)].

In Step 3, three numerical techniques are provided to obtain quasiparticle properties: (i) Fitting the VAFs to an analytical function, Eq. (5), (ii) Fourier transforming (FT) Appendix A VAFs, and (iii) using the maximum entropy method (MEM) Appendix B. Also, we note that Step 4, critical to obtaining anharmonic phonon dispersions and free energies, is missing from a similar work [13].

2. Description of the program

The phq package folder is contained in the compressed phq.zip file. Inside the folder, there are LICENSE file, README.md file and three sub-folders. There is an example of diamond Si in the example sub-folder. Four makefiles are in the system sub-folder. makefile_linux is for Linux or macOS operating systems and makefile_windows is for Windows operating system. Makefiles for both gfortran and ifort compilers are also prepared. ifort compiler is recommended for faster running speed and smaller memory requirement. One can modify properly the FC flag to enable other compilers.

The source code is in the src sub-folder with three Fortran90 files: configure.f90 contains three auxiliary modules, which configure the physical quantities, parameters and text read in settings. main.f90 is the main module where: (i) the mode-projected velocities are calculated from the MD trajectory; (ii) renormalized phonon frequencies and lifetimes are extracted from the mode-projected VAFs; (iii) effective harmonic force constants and thus anharmonic phonon dispersions are obtained. phq.f90 runs the program and records the running time. A detailed description of subroutines used in the main.f90 file is listed in Table 1.

After making the file, users need to put the phq executable into the same folder of those four input files in order to run the code. Run command ./phq < input to perform the calculation. The input files will be introduced in the Input files section. The code workflow is shown in Fig. 1.

3. Input files

There are 4 input files for the phq program: input, scf.out, dyn.out and md.out, which provide the general settings, structure, harmonic phonon, and MD information separately. Users can prepare the input files according to the example provided within the code package. The instructions for preparing the input files are as following:

3.1. input

input provides general settings for the calculation. The values of the parameters should be set by the user. The details of the parameters are described in Table 2.

3.2. scf.out

scf.out provides structure information of the primitive cell from self-consistent calculations. The values of the parameters should be same as those used in first-principles calculations. The details of the parameters are described in Table 3.
| Subroutine name    | Description                                                                                                                                 |
|-------------------|------------------------------------------------------------------------------------------------------------------------------------------------|
| control           | General control of the program.                                                                                                              |
| read_scf          | Read in structural information of the primitive cell.                                                                                       |
| read_md           | Read in MD information and compute atomic displacements from their static positions.                                                      |
| properties        | Compute the heat capacity via heat fluctuation. If no information other than atomic coordinates is provided in the md.out file, comment out this subroutine in the control subroutine. |
| read_dyn          | Read in harmonic phonon information, compute eigenmodes of the supercell and the primitive cell at different q-point and check the orthogonality. |
| harmonic_matrix   | Compute the harmonic force constant matrix from harmonic frequencies and harmonic eigenmodes.                                                |
| harmonic_force    | Compute the interatomic harmonic forces.                                                                                                      |
| frequency         | Compute the atomic velocities and perform velocity eigenmode projection, according to Eq. (2)(3).                                            |
| equipartition     | Compute the ionic kinetic energy from equipartition theorem.                                                                                  |
| correlation       | Compute the VAFs, according to Eq. (1).                                                                                                      |
| correlation_fit   | Fit the VAFs to Eq. (5) and obtain quasiparticle properties.                                                                                  |
| corr_fourier      | Perform FT of VAFs according to Eq. (4) and obtain quasiparticle properties.                                                                |
| corr_fit_fourier  | Perform FT of the fitted curves. Avoid calling this subroutine if shorter running time is desired.                                            |
| maximum_entropy   | Perform MEM calculation and obtain the quasiparticle properties.                                                                                |
| linear_response   | Obtain MEM power spectrum via linear prediction method.                                                                                       |
| lorentzian        | Obtain quasiparticle properties by performing a fitting of the MEM power spectrum to a Lorentzian function.                                    |
| gamma_matrix      | Compute the effective harmonic force constant matrix from renormalized frequencies and harmonic eigenmodes.                                  |
| gamma_force       | Compute the interatomic anharmonic forces.                                                                                                    |
| dynamics_matrix   | Compute the harmonic dynamical matrices from harmonic frequencies and harmonic eigenmodes. Comment out this subroutine if the effective harmonic dynamical matrices are desired. |
| dynamics_matrix_md| Compute the effective harmonic dynamical matrices from renormalized frequencies and harmonic eigenmodes, according to Eq. (6)(7)(8).            |
| write_dym         | Write down the effective harmonic dynamical matrices or the harmonic dynamical matrices with the same format of ph.x executable’s output, which can be read in by q2r.x executable in the Quantum ESPRESSO [16] suite to perform Eq. (9). |
Table 2: Parameters used in the input

| Parameter name     | Description                                                                                                                                 |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| dt                 | MD time step in atomic unit. If 1 fs time step is used, simply enter dt = 20.67055273.                                                        |
| step_md_use        | Number of MD steps needed for the calculation of mode-projected VAFs.                                                                           |
| correlation_time   | Desired decay time for VAFs in unit of dt.                                                                                                     |
| pole               | Parameter used in the MEM. It is used to filter high-frequency components. Usually a reasonable range of pole (200 ~ 2000) can yield smooth spectrum. |
| supercell          | Supercell used in MD related to the primitive cell. 3 integers are required to enter.                                                          |
| temperature        | MD temperature in unit of Kelvin.                                                                                                             |
| method             | Enter one of the integer number 0, 1 or 2 to select renormalized frequencies obtained by which method to compute the effective harmonic force constants and dynamical matrices. 0 represents the fitting approach (Eq. (5)). 1 represents the Fourier transformation. 2 represents the maximum entropy method. |

Table 3: Parameters used in the scf.out

| Parameter name    | Description                                                                                                                                   |
|-------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|
| ntype             | Number of different elements in the primitive cell.                                                                                           |
| natom             | Number of atoms in the primitive cell.                                                                                                       |
| mass              | Atomic mass of each element following the symbol of the element.                                                                             |
| lattice_parameter | Scale of lattice vectors in unit of Bohr radius.                                                                                               |
| cell_parameters   | Lattice vectors in cartesian coordinate in unit of lattice_parameter.                                                                         |
| atomic_positions  | Atomic positions of atoms in the primitive cell in reduced coordinates.                                                                     |
3.3. *dyn.out*

*dyn.out* provides harmonic phonon information. The format follows the *ph.x* executable’s output of the Quantum ESPRESSO [16] suite. Quantum ESPRESSO users can simply obtain the *dyn.out* file by: (i) Turn off the symmetry in the self-consistent calculations by *pw.x*. (ii) Do the harmonic phonon calculations by *ph.x*. (iii) Concatenate *dynmat1*, ..., *dynmatnq* together, where nq is the total number of the q-point. The details of the parameters are described in Table 4.

If other harmonic phonon calculation program is used, the *dyn.out* file should be prepared according to Table 4. It is further illustrated in Fig. 2, where the harmonic phonon information of the first q-point (Γ point) of diamond silicon is shown as an example. The yellow and blue parts are required and optional respectively as the program input while the green part is not required as input. Parameters that are required or optional need to be prepared by users, while parameters that are not required can be left blank. Note that the character strings Dielectric, Effective, Diagonalizing, q and freq are arguments that will be read in by the *phq* program and therefore should not be modified. Dielectric Tensor and Effective Charges are only needed to be provided in the harmonic phonon information of the first q-point.

3.4. *md.out*

*md.out* provides MD information. The initial atomic coordinates of the supercell before the MD run and the instantaneous atomic coordinates during the MD simulation need to be recorded. The details of the parameters are described in Table 5. Note that for either atomic positions or atomic_md_positions, atoms in each one primitive cell should be together instead of atoms of the same element being together. It is further illustrated in Fig. 3, which shows an example *md.out* file of 3 × 3 × 3 supercell of Pbnm MgSiO₃ in two formats. Fig. 3(a) takes the convention of Quantum ESPRESSO where atoms in one primitive cell are put together, while in Fig. 3(b), all Mg atoms, Si atoms and O atoms are put together. Here, format demonstrated in Fig. 3(a) should
Table 4: Parameters used in the dyn.out

| Parameter name | Description |
|----------------|-------------|
| q             | q-point in cartesian coordinates in unit of $2\pi/lattice_{parameter}$. This parameter is required. |
| freq          | Harmonic phonon frequencies. This parameter in unit of THz is required as program input as well as the following six columns of eigenvectors. Eigenvector of each atom has x, y and z components and each component has a real part and an imaginary part. The order of atoms should be the same as that of the atoms entered in atomic_positions in scf.out. |

Dielectric Tensor

Dielectric Tensor, which is a $3 \times 3$ matrix of real numbers. This parameter is optional, depending on whether LO-TO splitting needs to be considered in the system.

Effective Charges

Effective Charges, which are $3 \times 3$ matrices of real numbers for each of the atom. This parameter is optional, depending on whether LO-TO splitting needs to be considered in the system.

Dynamical matrix file

| atom # 2 | -1.140677552970 0.000001193733 0.000000248824 0.000001138321 -1.140677456367 -0.000001203593 0.000000160442 -0.000000861857 -1.140678533945 |
| atom # 1 | -0.113982806114E+01 0.587992782082E-06 -0.16691820747E-06 0.198030409404E-06 -0.113982272168E+01 -0.126084144858E-05 -0.21851522654E-06 -0.109703444124E-05 -0.113982838261E+01 |

Eigenvector of each atom has x, y and z components and each component has a real part and an imaginary part. The order of atoms should be the same as that of the atoms entered in atomic_positions in scf.out.

Effective Charges U-E: Z_{s(alpha)[beta]}

| atom # 1 | -0.113982806114E+01 0.587992782082E-06 -0.16691820747E-06 0.198030409404E-06 -0.113982272168E+01 -0.126084144858E-05 -0.21851522654E-06 -0.109703444124E-05 -0.113982838261E+01 |

Figure 2: Harmonic phonon information at Γ point of diamond silicon appears at the beginning of dyn.out file. The yellow part is required and the blue part is optional as phq program input, while the green part is not required and will not be read in by the program.
Table 5: Parameters used in the md.out

| Parameter name         | Description                                                                 |
|------------------------|------------------------------------------------------------------------------|
| total_step             | Total actual MD steps. In practice, recorded MD steps should be configurations after reaching thermal equilibrium and therefore less than this number. |
| atomic_positions       | Initial atomic positions in reduced coordinates of the supercell lattice vectors. |
| md_step                | Integer numbers of recorded MD steps, followed by the instantaneous atomic_md_positions in the MD simulation. |
| atomic_md_positions    | Atomic positions in reduced coordinates of the supercell lattice vectors during the MD simulation. |

be taken for md.out. Also, the order of atoms in each of the primitive cell should be in the same order as provided in scf.out. The way to extend the primitive to generate the supercell for the MD simulation can be determined by the users.

4. Output files

A detailed description of all the output files of phq program are summarized in Table 5. The main output files are frequency.freq, which records the renormalized frequencies, and dynamatmd1, ..., dynmatmdnq, which record the effective harmonic phonon information with the same format of ph.x executable’s output and can be read in by the q2r.x executable in the Quantum ESPRESSO suite. Anharmonic force constants, renormalized phonon dispersions, anharmonic entropy and free energy can be obtained from q2r.x executable’s output. If other Fourier interpolation program is used, either use the effective harmonic dynamical matrices file dynamical_matrix_md.mat or use the effective harmonic force constant matrix file gamma_matrix.mat to fit the format.

5. Example

Here we illustrate the performance of the phq code using diamond Si as an example. Anharmonic phonon dispersion, vibrational density of states, and anharmonic free energy are obtained. We use the density-functional theorem based Vienna ab initio simulation package (VASP) [17, 18] to carry out MD simulations on 4 × 4 × 4 supercells (128 atoms) of Si. We employ the generalized gradient approximation of Perdew, Burke, and Ernzerhof [19] and the projector-augmented wave method [20] with an associated plane-wave basis set energy cutoff of 320 eV. Simulations are carried out at the volume with a zero static pressure. Temperatures ranging from 300 K to 1500 K are controlled through the Nosé dynamics [21]. The MD runs for 50 ps with a time step of 1 fs. Harmonic phonons are calculated using density-functional perturbation theory (DFPT) [22].

5.1. Obtaining VAFs

The mode-projected VAFs, \( \langle V_{\mathbf{q}}(0)V_{\mathbf{q}}(t) \rangle \), are given by corr.vaf file. Fig. 4(a) displays the calculated \( \langle V_{\mathbf{q}}(0)V_{\mathbf{q}}(t) \rangle \) at several temperatures of the LA/LO mode at \( \mathbf{q} = \mathbf{W} \) ([1/4, 3/4, 1/2]). At each temperature, the VAF amplitude decays exponentially. Accordingly, its power spectrum obtained via a Fourier transformation (FT) of VAFs has a Lorentzian line shape with a main single peak, Fig. 4(c). This behavior demonstrates the validity of the concept of phonon quasiparticle
Figure 3: Atomic positions of $3 \times 3 \times 3$ supercell of $Pbnm$ MgSiO$_3$ are displayed in two formats: (a) Atoms that belong to the same primitive cell are put together. (b) Atoms of the same element are put together. $md$. out should take format (a) as $phq$ program input.
Table 6: Output files of the phq program

| Output               | Description                                                                                                                                 |
|----------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| corr.vaf             | VAF of each eigenmode of the supercell. The VAF of each eigenmode lies on each column following the correlation time on the first column.     |
| corr_fit.vaf         | Fitted exponentially decaying cosine functions (Eq. (5)) of correlation functions according to Green’s function from molecular dynamics \([2]\). The fitted curve of VAF of each eigenmode of the supercell lies on each column following the correlation time on the first column. |
| corr_fit_fourier.vaf | FT of the fitted VAF curves. The FT of fitted VAF curve of each eigenmode of the supercell lies on each column following their common frequency range lies on the first column. |
| corr_fourier.vaf     | FT of VAFs. The FT of VAF of each eigenmode of the supercell following its frequency range lie on every two columns.                          |
| dynamical_matrix_md.mat | Effective harmonic dynamical matrices. It is an assemble of all the effective harmonic dynamical matrices from dynmatmd1, ..., dynmatmdnq.                |
| dynmatmd0            | q-point list with the same format of ph.x executable’s output in the Quantum ESPRESSO suite. They are in cartesian coordinates in unit of \(2\pi/\text{lattice parameter}\). |
| dynmatmd1, ..., dynmatmdnq | Renormalized phonon information with the same format of ph.x executable’s output in the Quantum ESPRESSO suite. nq is the total number of the q-points. They share the same set of parameters of dyn.out. |
| frequency.freq       | Harmonic, fitted renormalized, FT renormalized and MEM renormalized phonon frequencies lie on the second, third, fourth and fifth column separately while the first column labels different eigenmodes of the supercell. |
| gamma_matrix.mat     | Effective harmonic force constant matrix, which are \(3 \times 3\) matrices of real numbers between each pair of atoms in the supercell.           |
| harmonic_matrix.mat  | Harmonic force constant matrix, which are \(3 \times 3\) matrices of real numbers between each pair of atoms in the supercell.                  |
| msd.out              | Mean square displacement of each atom in the supercell.                                                                                   |
| tau_fit.tau          | Phonon quasiparticle’s lifetime of each eigenmode of the supercell obtained by fitting the VAFs to Eq. (5).                                 |
| tau_fourier.tau      | Phonon quasiparticle’s lifetime extracted from the FT of VAF of each eigenmode of the supercell.                                           |
| tau_mem.tau          | Phonon quasiparticle’s lifetime extracted from the MEM power spectrum of each eigenmode of the supercell.                                |
| vector.out           | Eigenmodes of the supercell.                                                                                                              |
| vector_q.out         | Eigenmodes of the primitive cell at each q-point.                                                                                          |
and allows us to identify the renormalized phonon frequency ($\tilde{\omega}_{qs}$) and line width ($\tilde{\Gamma}_{qs}$) of the phonon mode. Note that the file recording the FT is corr_fourier.vaf.

In practice, however, it is not an optimal way to find $\tilde{\omega}_{qs}$ and $\tilde{\Gamma}_{qs}$ directly from the power spectrum obtained from FT. Instead, we fit the VAFs to an exponentially decaying cosine function \[ \frac{G_{qs}}{k_B T} \sim \text{VAF} \sim \text{exp}(-\frac{t}{\tau}) \cos(\tilde{\omega}_{qs} t + \phi) \] to extract $\tilde{\omega}_{qs}$ and $\tilde{\Gamma}_{qs}$, Eq. (5). From our previous work [10, 12, 11], $\tilde{\omega}_{qs}$ and $\tilde{\Gamma}_{qs}$ can be obtained by performing the fitting only for the first few oscillation periods of VAFs. Therefore, to do the fitting, one only needs to calculate VAFs for a relatively short correlation time. Note that the file recording the fitting is corr_fit.vaf.

The fitted curve at each temperature is shown in Fig. 4(b), matching the VAF very well. Our code also offers a way to obtain $\tilde{\omega}_{qs}$ by maximum entropy method (MEM) [15]. A list of $\tilde{\omega}_{qs}$ obtained by different methods can be found in the frequency.freq file. Users can choose renormalized frequencies obtained by fitting approach, FT or MEM to obtain the effective force constants and dynamical matrices by specifying 0, 1 or 2 for the method in the input file.

Figure 4: Mode-projected velocity autocorrelation functions (VAF) (grey) of the LA/LO mode at $\mathbf{q} = \mathbf{W}$ of diamond silicon at 300, 600, 900, 1200 and 1500 K respectively are shown in (a) and (b). The corresponding power spectra (blue) are shown in (c). (b) shows in red the curves fitted with Eq. (5) for comparison.
5.2. Obtaining frequency shifts

As a demonstration of the validity of the present approach, we compare the calculated thermal frequency shifts given by `frequency.freq` file with experimental measurements. Fig. 5(a)-5(c) display frequency shifts $\Delta \omega_q = \tilde{\omega}_q|_{V=V_{eq}} - \omega_q$ of a TO/LO mode at the $\Gamma$ point, TA and TO modes at the $X$ point ([0, 1/2, 1/2]), and at the $L$ point ([1/2, 1/2, 1/2]) at the equilibrium volume of zero static pressure. Because experiments were conducted under ambient pressure, the renormalized phonon frequencies obtained under constant volume conditions have to be corrected. We indicate that such correction can be properly captured by considering the thermal shifts caused by the temperature induced volume expansion [10],

$$\tilde{\omega}_q(T)|_{P=0} = \tilde{\omega}_q(T)|_{V=V_{eq}} + \omega_q[\exp(-\gamma_q\bar{\alpha}T) - 1],$$ (10)

where $\gamma_q$ is the mode Grüneisen parameter and $\bar{\alpha}$ is the temperature averaged thermal expansion coefficient:

$$\bar{\alpha}(T) = \frac{1}{T} \int_0^T \alpha(T')dT'.$$ (11)

The mode Grüneisen parameter connects the phonon frequency variation with the volume expansion and can be obtained by DFPT [22]. It is defined as [23]:

$$\gamma_q = -\frac{d \ln \omega_q(T)}{d \ln V(T)}.$$ (12)

In practice the weak temperature dependence can be ignored [24]:

$$\gamma_q = -\frac{d \ln \omega_q(0)}{d \ln V(0)},$$ (13)

where $\omega_q(0)$ is the harmonic phonon frequency at volume $V(0)$. $\alpha(T)$ is the thermal expansion coefficient which can be obtained by QHA. It is defined as:

$$\alpha(T) = \frac{1}{V(T)} \frac{dV}{dT}.$$ (14)

With this, according to Eq. (11), the temperature averaged thermal expansion coefficient can be obtained:

$$\bar{\alpha}(T) = \frac{1}{T} \ln \frac{V(T)}{V(0)}.$$ (15)

Overall, our calculated $\Delta \omega_q|_{P=0} = \tilde{\omega}_q|_{P=0} - \omega_q$ are in good agreement with experiments [25, 26], Fig. 5(d)-5(f). We note that at the $X$ point, TA and TO modes have similar frequency shifts at constant volume. After the incorporation of the volume expansion, i.e., at constant pressure, their frequency shifts differ significantly. This is essentially caused by the different Grüneisen parameters of these two modes.

5.3. Obtaining temperature dependent phonon dispersion

Temperature dependent renormalized phonon frequencies obtained as such are only for those few $q$-points sampled by MD simulations, which are not sufficient to converge the calculation of thermal properties. Nevertheless, these frequencies provide a basis to obtaining phonon frequencies at $q$-points throughout the Brillouin zone. Here, we rely on an effective harmonic dynamic matrix,
Figure 5: Temperature dependent frequency shifts $\Delta \omega_{qs}$ of diamond Si with a volume where the static pressure is zero of: (a) TO/LO mode at $\Gamma$, (b) TA and TO mode at $X$, and (c) TA and TO mode at $L$ high-symmetry point. (d)-(f) show the corresponding corrected frequency shifts at zero pressure, $\Delta \omega_{qs}|_{P=0}$, at different temperatures. Experimental results obtained by Raman spectra [25, 26] are shown for comparison.

Eq. (6), and the derived effective harmonic force constants, Eq. (7), which give us the effective harmonic dynamic matrix at arbitrary $q$-points via a Fourier interpolation, Eq. (8) [10].

To construct the effective harmonic dynamic matrix along this line, users first find files of dy

matmd0, dy

matmd1, ..., dy

matmd64 given by phq, and copy them to the phq/example/Si/postprocessing sub-folder. Files q2r.in, dispersion.in and plotband.in files are also there. Next run:

```
q2r.x < q2r.in > q2r.out
matdyn.x < dispersion.in > dispersion.out
plotband.x < plotband.in > plotband.out
```

to calculate anharmonic phonon dispersion of diamond silicon, where matdyn.x and plotband.x are also Quantum ESPRESSO executables.

Fig. 6 (a) displays the obtained anharmonic phonon dispersions at 600 K and 1200 K. The harmonic phonon dispersions calculated by DFPT at static zero-pressure equilibrium volume is also shown for comparison. It can be seen that the temperature effect on phonon frequencies is discernible, and the overall trend is that phonon frequencies decrease as temperature increases [28]. Accordingly, the major peaks of the obtained vibrational density of states (VDoS) shift to lower frequencies with increasing temperature, Fig. 6 (b). Note that the VDoSs are calculated with a $20 \times 20 \times 20$ $q$-point grid, equivalent to a supercell of 16000 atoms in a direct MD simulation, which is well beyond the capability of ab initio methods.

5.4. Obtaining anharmonic vibrational entropy and free energy

With the renormalized phonon frequencies, the entropy is obtained by an integration over the whole Brillouin zone [6],

$$S = k_B \sum_{q} (n_{qs} + 1) \ln(n_{qs} + 1) - n_{qs} \ln n_{qs},$$  

(16)
where \( n_{qs} = [\exp(\hbar \tilde{\omega}_{qs}/k_B T) - 1]^{-1} \). The free energy is obtained by numerical integration [10]:

\[
F(T) = E_0 + \frac{1}{2} \sum_{qs} \hbar \omega_{qs} - \int_0^T S(T')dT',
\]

where \( E_0 \) is the static ground state energy and \( \omega_{qs} \) is the harmonic phonon frequency.

It can be seen that \( \omega_{qs} \) is key quantity to calculate \( S \) and \( F \). To obtain \( \omega_{qs} \) over the whole Brillouin zone, users copy the dynmatmd0, dynmatmd1, ..., dynmatmd64 files obtained from phq to the phq/example/Si/postprocessing/vdos sub-folder. q2r.in and vdos.in files are also there. Then, run:

\[
\text{q2r.x < q2r.in > q2r.out}
\]

\[
\text{matdyn.x < vdos.in > vdos.out}
\]

to calculate anharmonic VDoS of diamond silicon on a \( 20 \times 20 \times 20 \) \( q \)-point grid. \( S \) and \( F \) can be readily obtained from output VDoS file vdos according to Eq. (16)(17).

Fig. 7 compares \( S \) and \( F \) obtained with different \( q \)-grids: \( 4 \times 4 \times 4 \) and \( 20 \times 20 \times 20 \). The discernible differences \( \Delta S \), Fig. 7(a), and thus \( \Delta F \), Fig. 7(b) reveal that it is necessary to use a sufficiently large number of \( q \)-point in order to converge thermal properties.
Figure 7: (a) Vibrational entropy ($S$) and (b) vibrational free energy ($F$) of diamond Si at volume with zero static pressure calculated with different $q$-grids: $4 \times 4 \times 4$ and $20 \times 20 \times 20$. Inserts: (a) Differences in vibrational entropy ($\Delta S$) and (b) vibrational free energy ($\Delta F$) obtained with $4 \times 4 \times 4$ and $20 \times 20 \times 20$ $q$-grids.
6. Conclusion

In this communication we report phq, a code for extracting phonon quasiparticle properties, obtaining temperature dependent renormalized phonon dispersions, and calculating anharmonic free energies from harmonic phonon calculations and MD simulations. The program can be installed on Linux, macOS and Windows operating systems. Outputs from VASP [17, 18] and Quantum ESPRESSO [16] are both accepted as inputs here. Extension of compatibility with ABINIT [29], LAMMPS [30], Phon [31] and Phonon [32] for phonon dispersions processing are planned for the near future.

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Appendix A Fourier transformation

The Fourier transformation (FT) of function $c(t)$ ($t \geq 0$),

$$C(\omega) = \int_0^\infty c(t)e^{i\omega t}dt \quad (18)$$

is done by mapping the $N$ consecutive evenly sampled points in the time domain to the frequency domain

$$D_k = \sum_{j=0}^{N-1} c_j \omega_j e^{i2\pi jk/N} \quad k = 0, ..., N - 1, \quad (19)$$

where $\omega_j$ is the window function. Then the discrete power spectrum is defined at $N$ nonnegative frequencies as

$$P(f_k) = \frac{1}{N} \sum_{j=0}^{N-1} |D_k|^2. \quad (20)$$

$f_k$ is defined only for the zero and positive frequencies

$$f_k = \frac{k}{N\Delta} = f_c \frac{k}{N} \quad k = 0, ..., N - 1, \quad (21)$$

where $f_c$ is the upper limit of the frequency, known as Nyquist frequency. The actual frequency range considered in the calculation is limited by the window function. In phq program, by default the upper limit of the window function of each mode is set to be integral period where the amplitude of the velocity autocorrelation function (VAF) drop to 0.75 of its maximum. This value can be modified by users in subroutine correlation of the main.f90 file. By default, rectangular window function is used

$$\omega_j = 1 \quad j = 0, ..., N - 1, \quad (22)$$
which is ready to obtain power spectrum of Lorentzian line shape. To avoid frequency leakage into
neighboring bins, Hann window is also provided
\[ \omega_j = \sin \left[ \frac{\pi (N-j)}{2N} \right]^2 \quad j = 0, ..., N - 1. \]  
(23)

Users can enable Hann window in subroutine `corr_fourier`.

**Appendix B  Maximum entropy method**

Maximum entropy method (MEM) is also known as all-poles model, autoregressive model,
which is used to obtain smooth power spectrum in signal processing. Here we assume that the
power spectrum of each mode follows the approximation
\[ P(f) = \frac{a_0}{\left| 1 + \sum_{j=1}^{N} a_j e^{i2\pi f \Delta j} \right|^2}, \]  
(24)
where \( a_0 \) as well as \( a_j \) is a set of coefficients of this approximation and \( \Delta \) is the sampling interval
in the time domain. \( a_0 \) and \( a_j \) can be obtained from linear prediction method (LP) \[14\]

\[ y_n = \sum_{j=1}^{M} a_j y_{n-j} + x_n \]  
(25)
where \( y_n \) are a series of input and also predicted values by the LP, \( x_n \) is the discrepancy between
the data and the predicted value. Here we use the polarized velocities as the input of LP. A
recursive procedure called Burg method \[14\] is adopted to minimize the discrepancy \( x_n \), which is
performed in subroutine `linear_response` of the `main.f90` file. Regarding it to take input \( x_n \) into
output \( y_n \), LP has a filter function
\[ H(f) = \frac{1}{1 - \sum_{j=1}^{M} d_j e^{i2\pi f \Delta j}} \]  
(26)
Thus, the power spectrum of the \( y_n \) equals the power spectrum of the \( x_n \) multiplied by \( |H(f)|^2 \).
Therefore, the coefficients \( a_0 \) and \( a_j \) can be related to the LP coefficients by
\[ a_0 = xms, \quad a_j = -d(j) \quad j = 1, ..., N. \]  
(27)
Then the MEM power spectrum can be obtained from Eq. (24). Phonon quasiparticle properties
are extracted from the power spectrum, which is done in subroutine `maximum_entropy`. A fitting
of the MEM power spectrum of each mode to a Lorentzian line shape performed in subroutine `lorentzian` also give quasiparticle properties for comparison.

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