



Editor's Choice

An efficient ab-initio quasiharmonic approach for the thermodynamics of solids



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ABSTRACT

A first-principles approach called the *self-consistent quasiharmonic approximation* (SC-QHA) method is formulated to calculate the thermal expansion, thermomechanics, and thermodynamic functions of solids at finite temperatures with both high efficiency and accuracy. The SC-QHA method requires fewer phonon calculations than the conventional QHA method, and also facilitates the convenient analysis of the microscopic origins of macroscopic thermal phenomena. The superior performance of the SC-QHA method is systematically examined by comparing it with the conventional QHA method and experimental measurements on silicon, diamond, and alumina. It is then used to study the effects of pressure on the anharmonic lattice properties of diamond and alumina. The thermal expansion and thermomechanics of $\text{Ca}_3\text{Ti}_2\text{O}_7$, which is a recently discovered important ferroelectric ceramic with a complex crystal structure that is computationally challenging for the conventional QHA method, are also calculated using the formulated SC-QHA method. The SC-QHA method can significantly reduce the computational expense for various quasiharmonic thermal properties especially when there are a large number of structures to consider or when the solid is structurally complex. It is anticipated that the algorithm will be useful for a variety of fields, including oxidation, corrosion, high-pressure physics, ferroelectrics, and high-throughput structure screening when temperature effects are required to accurately describe realistic properties.

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1. Introduction

Accurately simulating various anharmonic properties, i.e., thermal expansion and thermomechanics, of solids is important for obtaining a deep understanding of their plentiful thermal behaviors and for their realistic applications. The anharmonic properties can be derived from the volume and temperature dependences of the phonon spectra calculated using density-functional theory (DFT) [1]. The most popular approach is the quasiharmonic approximation method (QHA) [2–4], where only the volume dependence is considered for the phonon anharmonicity, and temperature is assumed to indirectly affect phonon vibrational frequencies through thermal expansion. Here, the phonon spectra of about ten or more volumes are usually required for a typical QHA simulation, and the thermal expansion and thermomechanics are derived by fitting the free energy-volume relationship. In some cases, e.g., at high temperatures, high-order anharmonicity caused by multi-phonon coupling cannot be omitted as in the QHA method, and some more complicated and

time-consuming methods, e.g., molecular dynamics [5–12], self-consistent ab initio lattice dynamics [13,14], perturbative/nonperturbative renormalized harmonic approximations [15–18], and vibrational self-consistent field calculations [19], can be used to obtain the temperature-dependent phonons. Nonetheless, approximately ten or more volumes of such phonon spectra are also required to accurately calculate the thermal expansion and thermomechanics with the high-order anharmonicities.

Phonon calculations based on DFT forces are always time consuming, and prior to the actual calculation, various computational parameters [1,20] also need to be carefully tested to ensure convergence of the vibrational frequencies and anharmonicity, including the pseudopotentials, cutoff energy, k -mesh density, energy and force convergence thresholds, and supercell size in the small-displacement method [21,22] or the q -mesh density in the density-functional perturbation theory approach [23,24]. The general rule-of-thumb requiring ten or more volumes will make the anharmonic simulation, even when utilizing the simplest QHA method, rather computationally expensive, especially in some condensed matter fields where a large number of structures must be considered or the compound under study has a large unit cell, low symmetry, and numerous inequivalent atoms:

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- (i) In the fields of solid oxidation and corrosion, there are always many compounds (elements, oxides, hydroxides, oxyhydroxides, etc.) to consider [25–30] and each composition may have many polymorphs [31–33].
- (ii) In the high-pressure physics field, not only a wide range of volumes but also a large number of complex phases should be examined [34–36].
- (iii) For the metallic alloys field, the thermodynamics and mechanics of many phases at variable composition and temperature are always of concern [37–39].
- (iv) In the perovskite oxides [40–42], ternary ceramics exhibit complex structures and large unit cells. The phonon calculations for an individual structure is already quite time consuming, not to mention the calculation of anharmonic properties in low-symmetry polymorphs.
- (v) In high-throughput screening and materials design [43–46] when including temperature effects, a huge number of compositions and structures should be calculated with a high efficiency-to-accuracy ratio.

To this end, these diverse fields require an efficient method to accelerate the investigation of the anharmonic properties of related solids at finite temperatures.

In this work, we formulate an *ab initio* method, called the *self-consistent quasiharmonic approximation* (SC-QHA) method, for achieving fast anharmonic calculations with high accuracy within the quasiharmonic approximation. Only the phonon spectra of two or three volumes are required in a SC-QHA calculation, which usually is much faster than the conventional QHA method. We carefully test the SC-QHA method using prototypical silicon, diamond, and alumina, and then also study the pressure effect on the anharmonic properties of diamond and alumina. Finally, we apply the SC-QHA method to accurately calculate the thermal expansion and thermomechanics of the structurally complex hybrid-improper ferroelectric $\text{Ca}_3\text{Ti}_2\text{O}_7$. Apart from the high efficiency, we show that the SC-QHA method is also very convenient for deciphering the microscopic physical origins of lattice dynamical and thermodynamic phenomena. Moreover, it can be readily transferred beyond the quasiharmonic realm to speed up the accurate first-principles simulation of thermal effects for the benefit of multiple fields in condensed-matter physics.

2. Thermodynamics and computation

2.1. Theoretical basis

The total Gibbs free energy ($G_{\text{tot}} = F_{\text{tot}} + PV$) of a crystal unit cell is expressed as

$$G_{\text{tot}}(P, T) = F_e(V, T) + F_{\text{ph}}(V, T) + PV, \quad (1)$$

where $P, V = V(P, T)$, and T are the external pressure, unit-cell volume, and temperature, respectively; F_e and F_{ph} are the electronic and phononic Helmholtz free energies, respectively. To conveniently present the basic algorithm and efficiency of the SC-QHA method, only nonmagnetic insulators are considered here, where the electronic excitation and magnetic excitations are neglected. The transferability of the SC-QHA algorithm for solids with more complex degrees of freedom are discussed below. Therefore, $F_e(V, T)$ here equals the electronic energy $E_e(V)$ calculated from density functional theory (DFT) and $F_{\text{ph}}(V, T)$ is expressed as

$$F_{\text{ph}} = \frac{1}{N_q} \sum_{q,\sigma} \left\{ \frac{\hbar\omega_{q,\sigma}}{2} + k_B T \log \left[1 - \exp \left(-\frac{\hbar\omega_{q,\sigma}}{k_B T} \right) \right] \right\}, \quad (2)$$

where k_B is the Boltzmann constant, N_q is the number of considered reciprocal q points ($\frac{1}{N_q}$ is the weight of each q point), and $\omega_{q,\sigma}$ is the

vibrational frequency of the σ -th phonon branch at the reciprocal coordinate q .

The equilibrium state under a specified external pressure P fulfills the relationship

$$\left. \frac{\delta G_{\text{tot}}}{\delta V} \right|_{P,T} = 0. \quad (3)$$

Combining Eqs. (1)–(3), we obtain an expression for the unit-cell volume

$$V(P, T) = \left[\frac{dE_e(V)}{dV} + P \right]^{-1} \times \frac{1}{N_q} \sum_{q,\sigma} U_{q,\sigma} \gamma_{q,\sigma}, \quad (4)$$

where $U_{q,\sigma}$ and $\gamma_{q,\sigma} = -\frac{V}{\omega_{q,\sigma}} \frac{d\omega_{q,\sigma}}{dV}$ are the internal energy and Grüneisen parameter of the phonon mode (q, σ). (To guarantee that γ is calculated from the phonon modes with the same symmetry, $k \cdot p$ theory is used to identify and match the phonon branches obtained from different volumes according to the similarity of each mode's eigenvector [47].) The physics underlying Eq. (4) is due to the balance between the external pressure P and internal pressure, i.e., electronic pressure ($P_e = -\frac{dE_e}{dV}$) plus the anharmonic phonon pressure ($P_\gamma = -\frac{dF_{\text{ph}}}{dV} = \frac{1}{VN_q} \sum_{q,\sigma} U_{q,\sigma} \gamma_{q,\sigma}$), such that

$$P = P_e(V) + P_\gamma(V, T). \quad (5)$$

In the quasiharmonic approximation [2–4], ω only depends on V such that the ω - V relationship can be described by a Taylor expansion (up to second order) as

$$\omega(V) = \omega(V_0) + \left(\frac{d\omega}{dV} \right)_0 \Delta V + \frac{1}{2} \left(\frac{d^2\omega}{dV^2} \right)_0 \Delta V^2, \quad (6)$$

where V_0 is the reference volume and $\Delta V = V - V_0$. Then, we can derive the volume dependence of γ as

$$\gamma(V) = -\frac{V}{\omega} \left[\left(\frac{d\omega}{dV} \right)_0 + \left(\frac{d^2\omega}{dV^2} \right)_0 \Delta V \right]. \quad (7)$$

The calculation of the n th order derivative of ω (i.e., $d^n\omega/dV^n$) requires the phonon spectra of $n+1$ volumes. With Eqs. (4), (6), and (7), the temperature-dependent unit-cell volume can be obtained in a self-consistent manner and it is this formalism which we call herein the self-consistent quasiharmonic approximation (SC-QHA) method. The complete derivation steps for the SC-QHA method, as well as the formula in the next section, can be found in the online [Supplemental Material](#).

The SC-QHA method can also be viewed as an improved nonlinear Grüneisen model that is implemented in a self-consistent way. In a conventional Grüneisen model [48–51], the linear ω - V relationship usually is considered, and during the calculation of the thermal-expansion coefficient $\alpha = \frac{1}{V} \frac{dV}{dT}$, the parameters V, ω , and γ are treated as constant. In addition, the zero-point vibration contribution to V is also absent in the Grüneisen model for $\alpha(T)$. Although a similar nonlinear ω - V relationship as that given in Eq. (6) has been used by Debernardi et al. for $\alpha(T)$ before [52], the contribution of zero-point vibrations to V were omitted. Herein, both the zero-point vibrational contribution and nonlinear ω - V relationship are treated in the SC-QHA method (by Eqs. (4) and (6)).

In principle, when we have an analytical expression for $\omega(V)$ (Eq. (6)), $V(P, T)$ could be directly derived by minimizing the analytical G_{tot} (Eq. (1)) with respect to V prior to using Eq. (4). This approach should have a comparable numerical efficiency as the self-consistent method. However, the SC-QHA method is a very convenient analytics tool for which considerable physical information (as present in Eq. (4)) can be obtained through the

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