

Calculating the anharmonic free energy from first principles

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(Received 8 January 2010; revised manuscript received 1 April 2010; published 7 May 2010)

We developed a method to calculate the anharmonic free energy without requiring any adjustable parameter. The requisite computations are first-principles quasiharmonic calculations plus an additional Canonical (NVT) ensemble first-principles molecular-dynamics simulation and, therefore, are affordable. The thermodynamic properties of diamond and MgO at high temperature improve substantially after including the anharmonic free energy.

DOI: [10.1103/PhysRevB.81.172301](https://doi.org/10.1103/PhysRevB.81.172301)

PACS number(s): 65.40.-b

With the development of density-functional theory (DFT) calculation, it is routine now to calculate the phonon density of state of the materials.¹ The free energy and hence thermodynamic properties can be calculated by using quasiharmonic approximation (QHA), where the phonon frequency only depends on the volume. Obviously, QHA ignores the intrinsic phonon-phonon interaction, namely, anharmonicity, which will lead to the pure temperature dependence of the phonon frequency. Since the anharmonicity becomes prominent at high temperature, DFT calculation combining QHA will not be enough good to predict the high-temperature thermodynamic properties although it works well at relative low temperature. For example, DFT calculation combining QHA can predict a thermal expansion, one of the properties most related to anharmonicity, much larger or smaller than the experimental data at high temperature.^{2,3}

Although anharmonicity has been widely studied, the calculation of the anharmonic free energy is still not trivial. Direct calculation by first-principles molecular-dynamics (FPMD) simulation is very expensive even with recent development.⁴ Most of other methods (see references in Ref. 5) inevitably need to introduce several adjustable parameters, which are hard to determine either by experiment or by theory. In order to combine smoothly with DFT calculation, where no adjustable parameters are needed, a method without requiring any adjustable parameter and with affordable time will be highly preferred in calculating anharmonic free energy.

Recently Wu and Wentzcovitch⁵ developed a method requiring only an unknown constant C , which can be determined easily by comparing the thermodynamic properties with the experimental data. The method produces the correct high- and low-temperature behavior of the anharmonic free energy. The thermodynamic properties of MgO from this method agree excellently with the experimental data to several thousand kelvin.⁵ Here we further developed a method to calculate the constant C using the FPMD simulation. The FPMD simulation in diamond and MgO directly confirmed our previous assumption⁵ that C is volume- and temperature-insensitive variable and can be assumed as constant. We are able to determine C from one FPMD simulation and get the volume and temperature dependence of the anharmonic free energy. The thermodynamic properties of MgO and diamond improve considerably after including the anharmonic free energy.

The temperature dependence of phonon frequency, the

consequence of the anharmonicity, is expressed in implicit way in Wu and Wentzcovitch's method,⁵

$$\Omega(V, T) = \omega(V'), \quad (1)$$

where ω is the phonon frequency from the first-principles calculations and Ω is the temperature-dependent phonon frequency used in quasiharmonic formula of the free energy. Ω is not the renormalized phonon frequency, which can be applied only in quasiharmonic entropy formula. The relation of Ω with the renormalized phonon frequency was discussed in Ref. 5. The temperature dependence of Ω is described by the temperature dependence of V' at a fixed volume V ,

$$V' = V \left[1 - C \frac{(V - V_0)}{V_0} \right], \quad (2)$$

where, C is a constant, V and V_0 are the predicted quasiharmonic volumes at high and zero temperature under the same quasiharmonic pressure. $V - V_0$ is the volume expansion caused by temperature at the pressure P . The two features of the anharmonicity, the anharmonicity (I) increases with temperature, and (II) decreases with pressure, are embodied in the term $(V - V_0)/V_0$. This is why the method works well while there is only one constant C .⁵ The anharmonic free energy F_{anh} is easily found to be

$$F_{anh}(V, T) = [F_H(V', T) - U_0(V')] - [F_H(V, T) - U_0(V)], \quad (3)$$

where F_H is quasiharmonic Helmholtz free energy and U_0 is internal static energy with

$$F_H(V, T) - U_0(V) = \frac{1}{2} \sum_{q,j} \hbar \omega_{q,j}(V) + k_B T \sum_{q,j} \ln \{ 1 - \exp[-\hbar \omega_{q,j}(V)/k_B T] \}. \quad (4)$$

The anharmonic free energy can also be calculated through the molecular-dynamics simulation by the thermodynamic integration,

$$\frac{F_{anh}(V,T)}{(N-1)k_B T} = - \int_0^T \frac{dT'}{T'} \left[\frac{[\langle U(T',V) \rangle - U_0(V)] - [\langle U_{qh}(T',V) \rangle - U_0(V)]}{(N-1)k_B T'} \right], \quad (5)$$

where $U_0(V)$ is the minimal potential energy, $U(T', V)$ is the potential energy at temperature T' , and $U_{qh}(T', V)$ is the potential energy in QHA at temperature T' . The brackets refer to ensemble average. Taking derivative with respect to temperature and using high-temperature relation for the harmonic oscillator, $\langle U_{qh}(T, V) \rangle - U_0(V) = 1.5(N-1)k_B T$, we have

$$\frac{\partial}{\partial T} \frac{F_{anh}(V,T)}{(N-1)k_B T} = - \frac{A}{T} \quad (6)$$

with

$$A = \left[\frac{[\langle U(T,V) \rangle - U_0(V)]}{(N-1)k_B T} - \frac{3}{2} \right] \quad (7)$$

at the high temperature. A can be calculated from one NVT ensemble FPMD simulation and further used to determine C through Eqs. (3)–(6). We are also able to check our assumption that C is volume and temperature independence by conducting FPMD simulations at various temperatures and volumes. Two cases that we test show that C is volume and temperature insensitive. This means that one can get the volume and temperature dependence of the anharmonic free energy with only one NVT ensemble FPMD simulation.

Computations were performed using QUANTUM ESPRESSO, a package based on DFT, plane wave, and pseudopotential.⁶ The quasi-harmonic calculations of periclase, which the current calculations are based on, have been published earlier.^{2,7} The local-density approximation was used in the calculations. The pseudopotential for magnesium was generated by the method of von Barth and Car while that for oxygen was generated by the method of Troullier and Martins.⁸ The pseudopotential for carbon was generated by the method of Vanderbilt ultrasoft pseudopotential.⁹ The plane-wave cutoff energy is 70 Ry and 40 Ry for periclase and diamond, respectively. Brillouin-zone summations over electronic states

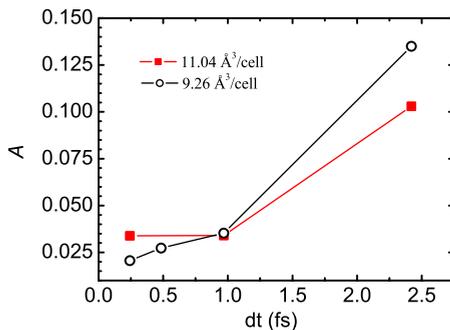


FIG. 1. (Color online) The dependence of A [see Eq. (7)] on time step dt at various volumes for diamond at 2000 K.

were performed over $4 \times 4 \times 4$ (10 points) k mesh with $(1/2, 1/2, 1/2)$ shift from origin. Dynamical matrices were computed on $4 \times 4 \times 4$ q mesh using density-functional perturbation theory¹ and then interpolated in a regular $12 \times 12 \times 12$ q mesh to obtain the vibrational density of state for periclase and diamond, respectively.

FPMD were performed in the cubic cell with 64 atoms for both periclase and diamond with the same pseudopotential, exchange-correlation functional, and cutoff energy as QHA calculations. The temperature is controlled by Andersen method.¹⁰ For each simulation, the first 1.5 ps simulation is used to evolve the system into the equilibration and another 3 ps simulation is found to be enough long to get the ensemble average. For example, A is almost unchanged (from 0.0353 to 0.0356) when we double the simulation time for diamond at volume $9.26 \text{ \AA}^3/\text{cell}$ with time step 1 fs

A [see Eq. (7)] is very sensitive to the ensemble average. 1 meV/atom difference in potential energy, which is usually acceptable for yielding the good dynamic, leads to the difference in A about 0.008. Therefore A can be dramatically affected by time step dt . Convergence check for dt was shown in Fig. 1. For diamond, 1 fs is enough to get the convergence result for volume at $11.04 \text{ \AA}^3/\text{cell}$. However a smaller time step than 1 fs might be needed for smaller vol-

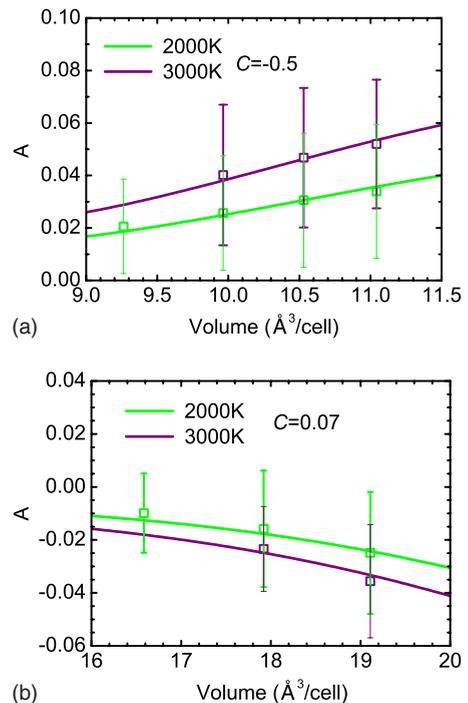


FIG. 2. (Color online) The dependence of A [see Eq. (7)] on volume at various temperatures for (a) diamond and (b) MgO. Results from FPMD simulation are shown in open squares with the errors.

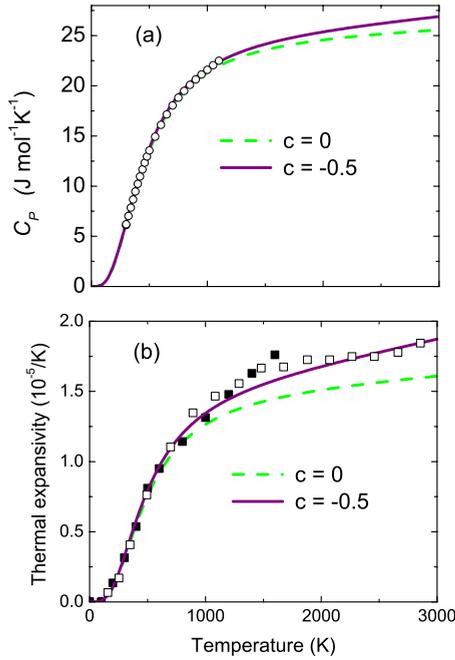


FIG. 3. (Color online) Thermodynamic properties of diamond at 0 GPa ($c=0$ correspond to QHA). (a) The heat capacity at the constant pressure and (b) the thermal expansion. Experimental data shown in open circles and solid squares are from Refs. 14 and 15, respectively. The results from path integral Monte Carlo simulation (Ref. 16) are shown in open squares.

ume. For example, a time step 0.25 fs is required to get convergence result for volume at $9.26 \text{ \AA}^3/\text{cell}$. Therefore, we should always check dt because a large dt can lead to a significant overestimation of A .

In Eq. (2) we assumed that volume and temperature dependence of the anharmonicity can be well described by term $(V-V_0)/V_0$ and C is a volume- and temperature-independent constant. The assumption is supported by several facts:⁵ (1) the systematic improvement in thermodynamic properties of MgO and Mg_2SiO_4 , (2) the correct low- and high-temperature behavior of the anharmonic free energy, and (3) the nonlinear temperature dependence of the phonon frequency at low temperature and the linear temperature dependence of the phonon frequency at high temperature, which has been observed by the Raman experiments.^{11,12} FPMD simulation here further confirmed directly that C is volume and temperature insensitive. As shown in Fig. 2, the calculated A with $C=-0.5$ for diamond are in good consistence with FPMD simulation results at various volumes and temperatures. This is also true for MgO. C for MgO determined by FPMD is 0.07 with uncertainty about ± 0.04 . This value is close to 0.1, a value derived from the experimental data and within the uncertainty of FPMD result. The anharmonic free energy at $18.68 \text{ \AA}^3/\text{cell}$ and 2000 K for MgO with $C=0.7$, 0.7 J/mol, agrees with Oganov and Dorogokupets's molecular-dynamics simulation result.¹³ All of these results clear indicated that Eq. (2) does capture the essence of the anharmonic free energy. Now we are able to get the C and further the volume and temperature dependence of the anharmonic free energy from first-principles QHA calculations

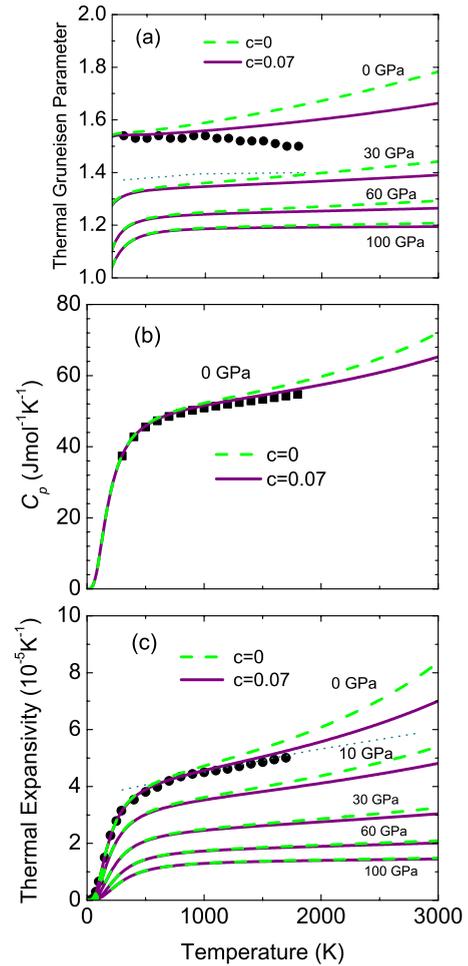


FIG. 4. (Color online) Thermodynamic properties of MgO ($c=0$ correspond to QHA). (a) The thermal Grüneisen parameter, (b) the heat capacity at the constant pressure, and (c) the thermal expansion. Experimental data shown in solid circles and solid squares are from Refs. 17 and 18, respectively. Results from molecular-dynamics simulation (Ref. 19) are shown in dotted lines.

and one NVT ensemble FPMD simulation. Namely, we developed a method to calculate the anharmonic free energy from first-principles calculations with affordable computation time.

Thermodynamic properties of diamond and MgO are shown in Figs. 3 and 4, respectively. QHA results are consistent with the previous calculations.^{2,3,7} The thermodynamic properties agree well with the experimental data at relative low temperature. But at high temperature, QHA significantly underestimates the thermodynamic properties of diamond, while it overestimates the thermodynamic properties of MgO. We had known in Ref. 5 that the calculated thermodynamic properties of MgO with $C=0.1$ agree excellently with the experimental data up to the highest temperature measured. Using the C derived from FPMD, 0.07, we are able to dramatically reduce the discrepancies in thermodynamic properties of MgO between the calculated result and the experimental data although we cannot remove completely the systematic deviations. For diamond, anharmonic correction improves significantly the thermodynamic proper-

ties. After correction, there are no systematic deviations between the calculated and measured heat capacity up to the highest temperature measured. Although the difference between the calculated and the measured thermal expansion is still large at $T > 1200$ K, the calculated thermal expansion of diamond is in good consistence with the path integral Monte Carlo simulation results¹⁶ up to 3000 K.

The materials can be divided into two types based on their anharmonicity. Those like MgO have the positive C and the positive anharmonic free energy. Their heat capacity at constant volume, C_V , is always below the Dulong-Petit limit. On the contrary, those like diamond have the negative C and the negative anharmonic free energy. Their C_V can crossover the Dulong-Petit limit at the certain temperature. Since the anharmonic free energy can be negative and positive, we can expect that the anharmonic free energy may be able to significantly affect the phase boundary especially in the case that the anharmonic free energy is positive at one phase and negative at another phase.

In summary, our assumption that the volume and temperature dependence of the anharmonicity can be well described by Eq. (2) with a constant C is confirmed by FPMD simulation in diamond and MgO. C can be determined with only one NVT ensemble FPMD simulation. Therefore, the anharmonic free energy can be obtained from first-principles calculation with the affordable computation time. The anharmonic free energy can be negative or positive, which may cause a noticeable effect on the phase boundary for some materials. Thermodynamic properties of diamond and MgO improve significantly at high temperature after including the anharmonic free energy.

The author thanks Renata Wentzcovitch for useful discussion. Computations were performed at University of Southern California using the 52.4 teraflops Linux cluster at the Research Computing Facility.

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