THINK INDIA JOURNAL

ISSN: 0971-1260

Vol-22-Issue-16-August-2019

A Short Review on *Ab-Initio* Quasi-Harmonic and Accelerated Quasi-Harmonic Methodologies To Compute Finite-Temperature Mechanical and Thermodynamic Properties For Solid Materials

Jewel Raj K. R.,[1]Vishajeet Singh Sekhon, [1]Ajit Kumar Sharma,[1] and Pinku Nath[1,*]

[1]School of Chemical Engineering and Physical Sciences,

Lovely Professional University, Phagwara, Punjab 144411, India

* pinku.24358@lpu.co.in

(Dated: December 3, 2019)

The quasi-harmonic approximation (QHA) method is an elegant technique and takes reasonably less computational time. For more than three decades QHA is being used successfully to compute properties such as thermal expansion, bulk modulus, specific heat, enthalpy of mixing and many other thermodynamic related properties. It is also used to estimate transport properties and phase transitions and also to explain negative thermal expansions. The mechanical properties of solids which are used to measure strength, hardness, and stability can be studied with QHA. QHA requires multiple phonon calculations which makes it inefficient to compute properties for large numbers of materials particularly in high-throughput material design. In order to make it more efficient in terms of computational time, some accelerated techniques have been developed. Along with the strengths, this review also addresses limitations of QHA.

INTRODUCTION:

The thermodynamic properties of materials are being used to design and engineer new materials [1, 2]. It can be computed in various ways, among them *ab-initio* molecular dynamics [3–5] and exciting atoms in supercell lattice dynamic methods [6–8] are the most trusted techniques. However, these are very time-consuming. The *ab-initio* quasi-harmonic Debye approach [9–11] is a faster method and the computed results match quite well with experiments, mostly for the monoatomic crystals. The QHA is an intermediate technique that doesn't take very large computational time and can be applied to all kinds of materials and predicted results fall in line with the experiments. Here, in thisarticle,we are reviewing the variety of works that have been performed both with QHA and accelerated QHA.

In QHA, the total free energy (F) of a system is written as sum of three terms (Eq. 1). These are vibration less total energy at 0 K (E_0), vibration free energy (F_{vib}), and free energy due to thermal electronic excitations (F_{elec}) [12–14]. The first term of the equation can be computed with *ab-initio* software [15, 16], the second term is computed by integrating over phonon density of states which is obtained using lattice dynamic method [17, 18]. The last term of the equation is

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

obtained by integrating over electronic density of states. Commonly, F is the function of both volume (V) and temperature (T).

$$F(V,T) = E_0(V) + F_{\text{vib}}(V,T) + F_{\text{elec}}(V,T), \quad (1)$$

Isotropic properties: Volumetric thermal expansion (α_V), specific heat (C_p) and such other isotropic properties are scalar which do not depend on crystallographic directions. These properties, at a given temperature, are computed by minimizing F with respect to V. Temperature is a parameter here. QHA has been applied to more than 130 materials comprising metallic and non-metallic crystal types. The results match with experimental data within 20% error bar (Figure 1).

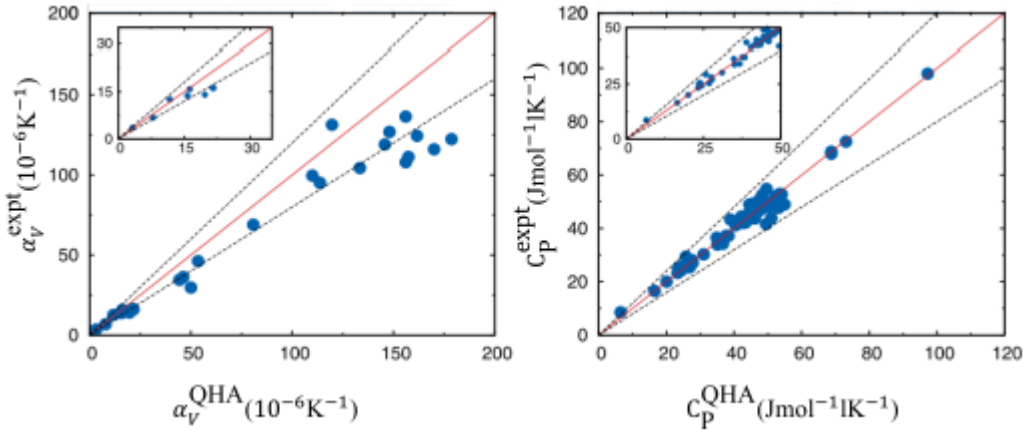

FIG. 1. The volumetric thermal expansion and specific heat values for more than 130 materials. The x-axis and y-axis are QHA and experimental data respectively. The dotted lines represent 20% error bar [17].

Anisotropic properties: While computing direction dependent properties, for example, coefficient of thermal expansion (α), F is used as the function of lattice vector. The properties computed with QHA is shown in Figure 4.

Negative thermal expansions: Generally, materials expand upon heating. However, there are some materials which shrink on heating and have negative α values. There are mainly two available mechanisms to explain the phenomenon [19]. QHA has been used to support these explanations. The negative thermal expansion values for Si and Cu_2O, for various temperature ranges, have been explained satisfactorily using QHA (Figure 2).

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

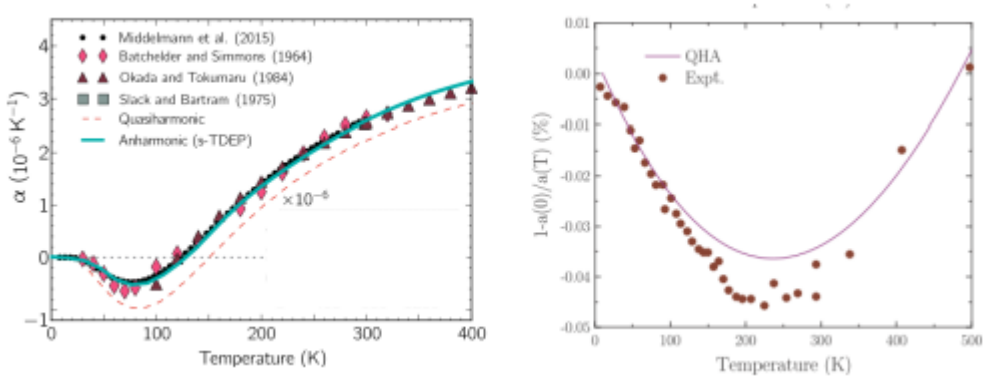

FIG. 2. Thermal expansion values for Si [20] and Cu_2O [21].

Mechanical properties: In the Voigt notation, stress (σ) and strain (ϵ) can be expressed as

$$\sigma_i = \sum_j^6 C_{ij}\epsilon_j \qquad (2)$$

whereCij is elastic stiffness constants of a crystal and it is a 6 × 6 matrix with Cij =Cji , so, the number of independent component components is 21 instead of 36. To extract Cij values the F in Eq. 2 is reformulated as a function of magnitude of strain δ, strain itself [22,23]

$$F(\delta,\epsilon,T) = E_0(\delta,\epsilon) + F_{\text{vib}}(\delta,\epsilon,T) + F_{\text{elec}}(\delta,\epsilon,T), \qquad (3)$$

The ϵ for various crystal systems are prescribed in terms of δ. For example, components ϵ for cubic system are (0, 0, 0, δ, δ, δ), (δ, δ, 0, 0, 0, 0), (δ, δ, δ, 0, 0, 0). The component Cij can be extracted by fitting the F in Eq. 3. The results mostly found consistent with experiments (Figure 3).

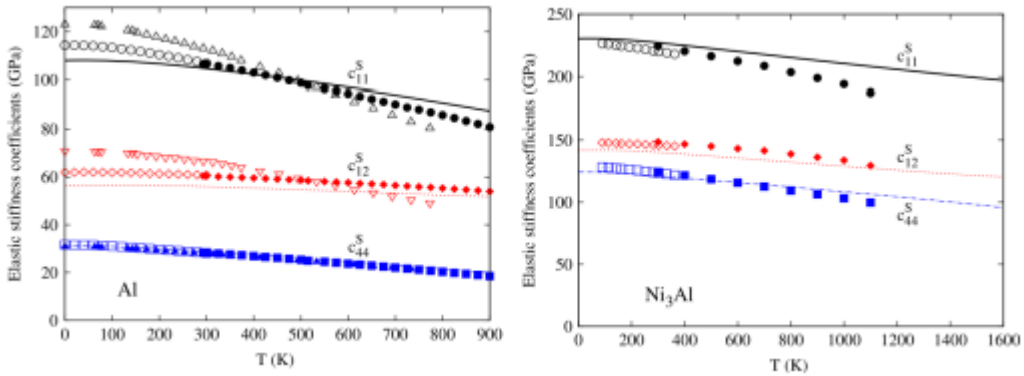

FIG. 3. T -dependent elastic constants for Al and Ni_3Al [24].

Accelerated QHA techniques: As mentioned earlier, F_{vib} is computed on various V values which requires as many lattice dynamic calculations. This makes QHA relatively expensive. In

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

accelerated QHA, two or three phonon calculations are performed and phonons are then extrapolated to any arbitrary values of V which reduces computational cost [25,26]. The results are consistent with QHA (Figure 4).

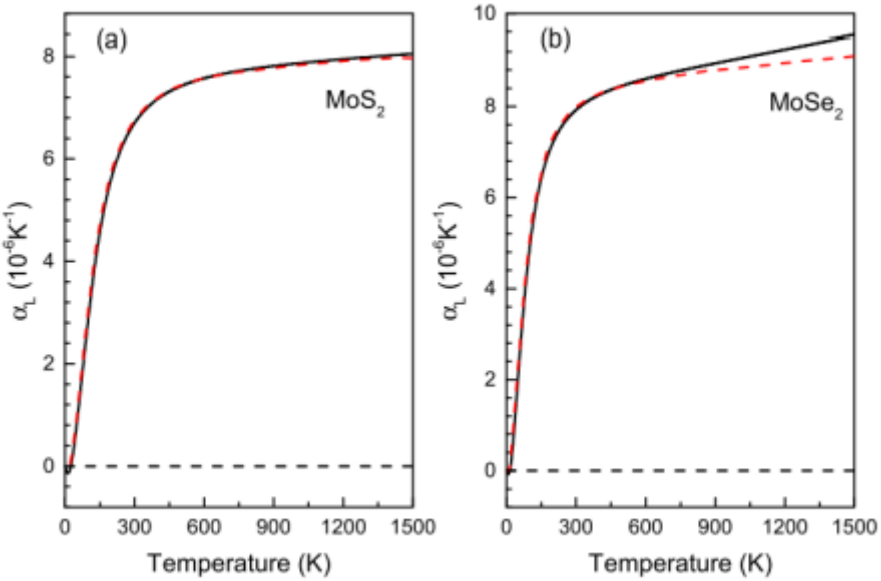

FIG. 4. Temperature dependent coefficients of thermal expansions for two materials [24]. The red and black lines represent QHA and accelerated QHA calculations.

Limitations of QHA: QHA has been consistently good to explain experimental findings for materials with different symmetries. However, it cannot be applied to materials unstable at the ground state. For example, most of the perovskites produce imaginary frequencies with lattice dynamics calculations and therefore, QHA can't be used. In addition to that, at high temperature near the melting point, QHA computed results show significant difference from experiments. In such cases, higher-order theories where temperature-dependent phonon are involved are useful.

CONCLUSIONS

In this review, we have discussed the QHA method along with accelerated methodologies that produce results as good as QHA. It is also discussed how the techniques are efficient in computing various properties. Finally, the limitations of QHA are also addressed with alternative solutions to handle the problem.

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

[1] Y. Zhuo, A. M. Tehrani, and J. Brgoch, "Predicting the Band Gaps of Inorganic Solids by Machine Learning", J. Phys. Chem. Lett. vol. 9, pp. 1668, Mar. 2018.

[2] K. T. Butler, D. W. Davies, H. Cartwright, O. Isayev, and A. Walsh, "Machine learning for molecular and materials science",Nature vol. 559, pp. 547, Jul. 2018.

[3] H. Yu, D. Duan, H. Liu, T. Yang, F. Tian, K. Bao, D. Li, Z. Zhao, B. Liu, and T. Cui, "Ab initio molecular dynamic study of solid-state transitions of ammonium nitrate", Sci. Rep. vol. 6, pp. 18918,Jan. 2016.

[4] G. Kresse and J. Hafner, "Ab initio molecular dynamics for open-shell transition metals",Phys. Rev. B vol. 48, pp. 13115–13118, Nov. 1993.

[5] H. L. Zhang, Y. F. Han, W. Zhou, Y. B. Dai, J. Wang, and B. D. Sun, "Atomic study on the ordered structure in Al melts induced by liquid/substrate interface with Ti solute", Appl. Phys. Lett. vol. 106, pp. 041606, Jan. 2015.

[6] P. Souvatzis, O. Eriksson, M. I. Katsnelson, and S. P. Rudin, "Entropy Driven Stabilization of Energetically Unstable Crystal Structures Explained from First Principles Theory", Phys. Rev. Lett. vol. 100, pp. 095901, Mar. 2008.

[7] I. Errea, M. Calandra, and F. Mauri, "First-Principles Theory of Anharmonicity and the Inverse Isotope Effect in Superconducting Palladium-Hydride Compounds", Phys. Rev. Lett. vol. 111, pp. 177002, Oct. 2013.

[8] O. Hellman and I. A. Abrikosov, "Temperature-dependent effective third-order interatomic force constants from first principles", Phys. Rev. B vol. 88, pp. 144301, Aug. 2013.

[9] M. A. Blanco, E. Francisco, and V. Lua˜na, "GIBBS: isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model", Comput. Phys. Commun. vol. 158, pp. 57–72, Mar. 2004.

[10] L.-T. Yeh and R. C. Chu, "Thermal Management of Microloectronic Equipment: Heat Transfer Theory, Analysis Methods, and Design Practices" (ASME Press, 2002).

[11] J.-P. Poirier, "Introduction to the Physics of the Earths Interior", (Cambridge University Press, 2000), 2nd edn.

[12] Z. K. Liu and Y. Wang, "Computational Thermodynamics of Materials", (Cambridge University Press, 2016), 1 edn.

[13] Y. Wang, Z.-K. Liu, and L.-Q. Chen, "Thermodynamic properties of Al, Ni, NiAl, and Ni_3Al from first-principles calculations", Acta Mater. vol. 52, pp. 2665–2671, May. 2004.

[14] T. Duong, S. Gibbons, R. Kinra, and R. Arr´oyave, "Ab-initio approach to the electronic, structural, elastic, and finite temperature thermodynamic properties of Ti_2AX (A = Al or Ga and X = C or N)", J. Appl. Phys. vol. 110, pp. 093504, Nov. 2011.

[15] G. Kresse and J. Furthm¨uller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set", Phys. Rev. B 54, 11169–11186, Oct. 1996.

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

[16] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo,A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo,G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials", J. Phys.: Condens. Matter vol. 21, pp. 395502, Sep. 2009.

[17] P. Nath, J. J. Plata, D. Usanmaz, R. Al Rahal Al Orabi, M. Fornari, M. BuongiornoNardelli, C. Toher, and S. Curtarolo,"High-throughput prediction of finite-temperature properties using the quasi-harmonic approximation", Comput. Mater. Sci. vol. 125, pp. 82–91, Mar. 2016.

[18] A. Togo and I. Tanaka, "First principles phonon calculations in materials science", Scr. Mater. vol. 108, pp. 1–5, Aug. 2015.

[19] W. Mille, C. W. Smith, D. S. Mackenzie, and K. E. Evans, "Negative thermal expansion: a review", J. Mater. Sci. vol. 44, pp. 5441, Jul. 2009.

[20] D. S. Kim, O. Hellman, J. Herriman, H. L. Smith, J. Y. Y. Lin, N. Shulumba, J. L. Niedziela, C. W. Li, D. L. Abernathy, and B. Fultz, "Nuclear quantum effect with pure anharmonicity and the anomalous thermal expansion of silicon", PNAS vol. 115, pp. 1992, Feb. 2018.

[21] J. Linnera, A. Erba, and A. J. Karttunen, "Negative thermal expansion of Cu_2O studied by quasi-harmonic approximation and cubic force-constant method", J. Chem. Phys. vol. 151, pp. 184109, Nov. 2019.

[22] M. Destefanis, C. Ravoux, A. Cossard, and A. Erba, "Thermo-Elasticity of Materials from Quasi-Harmonic Calculations", Minerals vol. 9, pp. 16, Dec. 2019.

[23] S. H. Zhang and R. F. Zhang, "AELAS: Automatic ELAStic property derivations via high-throughput first-principles computation", Comput. Phys. Commun. vol. 220, pp. 403, Aug. 2017.

[24] G. Liu, Z. Gao, and J. Ren, "Anisotropic thermal expansion and thermodynamic properties of monolayer β-Te", Phys. Rev. B vol. 99, pp. 195436, May. 2019.

[25] P. Nath, D. Usanmaz, D. Hicks, C. Oses, M. Fornari, M. B. Nardelli, C. Toher, and S. Curtarolo, "AFLOW-QHA3P: Robust and automated method to compute thermodynamic properties of solids", Phys. Rev. Mater. vol. 3, pp. 073801, Oct. 2019.

[26] L.-F. Huang, X.-Z. Lu, E. Tennessen, and J. M. Rondinelli, "An efficient ab-initio quasiharmonic approach for the thermodynamics of solids", Comput. Mater. Sci. vol. 120, pp. 84–93, Jul. 2016.