

RESEARCH ARTICLE | NOVEMBER 06 2023

Extreme sensitivity of higher-order interatomic force constants and thermal conductivity to the energy surface roughness of exchange-correlation functionals

Hao Zhou ; Shuxiang Zhou ; Zilong Hua ; Kaustubh Bawane ; Tianli Feng 



Appl. Phys. Lett. 123, 192201 (2023)

<https://doi.org/10.1063/5.0173762>



View
Online



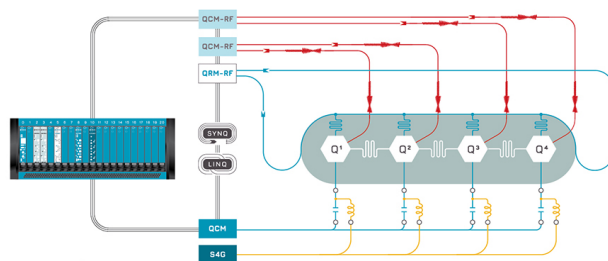
Export
Citation

CrossMark



Integrates all
Instrumentation + Software
for Control and Readout of

Superconducting Qubits
NV-Centers
Spin Qubits



Superconducting Qubit Setup

[find out more >](#)

Extreme sensitivity of higher-order interatomic force constants and thermal conductivity to the energy surface roughness of exchange-correlation functionals

Cite as: Appl. Phys. Lett. **123**, 192201 (2023); doi: [10.1063/5.0173762](https://doi.org/10.1063/5.0173762)

Submitted: 24 August 2023 · Accepted: 15 October 2023 ·

Published Online: 6 November 2023



View Online



Export Citation



CrossMark

Hao Zhou,¹  Shuxiang Zhou,²  Zilong Hua,²  Kaustubh Bawane,²  and Tianli Feng^{1,a)} 

AFFILIATIONS

¹Department of Mechanical Engineering, University of Utah, Salt Lake City, Utah 84112, USA

²Idaho National Laboratory, Idaho Falls, Idaho 83415, USA

Note: This paper is part of the APL Special Collection on Advances in Thermal Phonon Engineering and Thermal Management.

^{a)}Author to whom correspondence should be addressed: tianli.feng@utah.edu

ABSTRACT

In this Letter, we report that the fourth-order interatomic force constants (4th-IFCs) are significantly sensitive to the energy surface roughness of exchange-correlation (XC) functionals in density functional theory calculations. This sensitivity, which is insignificant for the second- (2nd-) and third-order (3rd-) IFCs, varies for different functionals in different materials and can cause misprediction of thermal conductivity by several times of magnitude. As a result, when calculating the 4th-IFCs using the finite difference method, the atomic displacement needs to be taken large enough to overcome the energy surface roughness, in order to accurately predict phonon lifetime and thermal conductivity. We demonstrate this phenomenon on a benchmark material (Si), a high-thermal conductivity material (BAs), and a low thermal conductivity material (NaCl). For Si, we find that the LDA, PBE, and PBEsol XC functionals are all smooth to the 2nd- and 3rd-IFCs but all rough to the 4th-IFCs. This roughness can lead to a prediction of nearly one order of magnitude lower thermal conductivity. For BAs, all three functionals are smooth to the 2nd- and 3rd-IFCs, and only the PBEsol XC functional is rough for the 4th-IFCs, which leads to a 40% underestimation of thermal conductivity. For NaCl, all functionals are smooth to the 2nd- and 3rd-IFCs but rough to the 4th-IFCs, leading to a 70% underprediction of thermal conductivity at room temperature. With these observations, we provide general guidance on the calculation of 4th-IFCs for an accurate thermal conductivity prediction.

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0173762>

Accurately predicting lattice thermal conductivity holds immense significance in a wide range of applications such as thermal management,¹ thermal barrier coatings,² and thermoelectric devices.³ Over the past years, first principles-based three- and four-phonon theories have emerged as the most reliable and widely accepted approaches for the lattice thermal conductivity prediction.^{4–8} In these methods, the harmonic (second-order) interatomic force constants (IFCs), or 2nd-IFCs, are used to calculate the phonon frequencies, velocities, and specific heat. The third- and fourth-order IFCs, or 3rd- and 4th-IFCs, are used to calculate the three- and four-phonon scattering rates, respectively. These quantities are implemented in the exact solution to the linearized Boltzmann transport equation (BTE) to predict the thermal conductivity.

To determine the IFCs, the most widely used method is the finite difference method (FDM)⁹ based on the density functional theory

(DFT)^{10,11} calculations. Thus, the precision of DFT calculations determines the accuracy of the predictions of IFCs and thermal conductivity. While DFT is an *ab initio* theory, which does not require any prior knowledge of the system or fitting parameters, its accuracy can be affected by many factors. Within DFT, the many-body problem of electrons is approximated by using the electron density distribution based on Kohn-Sham density functional theory.^{10,11} The total energy of the system can be expressed as the sum of kinetic energy, electron-ion interaction potential energy, electron-electron coulomb repulsive energy, and exchange-correlation (XC) energy.¹² The XC functional contains all the many-body quantum effects and must be known for any DFT calculations. Currently, commonly used XC functionals are local density approximation (LDA)¹³ and generalized gradient approximation (GGA) including Perdew-Burke-Ernzerhof

(PBE)¹⁴ as well as its revised version for solids (PBEsol).^{15,16} Several studies have been done to investigate the impact of different XC functionals on thermal conductivity as reviewed below.

Jain and McGaughey studied the effect of different XC functionals on thermal conductivity and phonon properties for isotopically pure crystalline silicon. They found the thermal conductivity at room temperature can be underestimated by up to 17% and overestimated by 12% depending on the choice of XC functionals.¹⁷ Qin *et al.* considered ten different XC functionals and obtained thermal conductivities of graphene, which varies from 1396 to 4376 W/mK. They found that it was the scattering rates of long-wavelength phonon modes with mean free path longer than 1000 nm that caused the diversity of thermal conductivities.¹⁸ Meanwhile, much higher thermal conductivities of graphene ranging from 5442 to 8677 W/mK were obtained by Taheri *et al.* by using different XC functionals and pseudopotentials.¹² In 2019, Arrigoni and Madsen found that even though LDA and PBE could predict the same thermal conductivity, they give different phonon velocities and scattering rates. LDA has stronger binding than PBE and, thus, predicts higher velocities (due to larger 2nd-IFCs) and higher scattering rates (due to larger 3rd-IFCs). In addition, Mortazavi *et al.* investigated the effect of XC functionals on the *ab initio* molecular dynamics (AIMD). They took advantage of machine learning potentials trained by the AIMD trajectories to extract 2nd and 3rd IFCs using FDM for graphene with three XC functionals, and they found that the effect of XC functionals on thermal conductivity is negligible.¹⁹ Dongre *et al.* found that the thermal conductivity of GaP varies from 83 to 153 W/mK by using LDA and PBE.²⁰ Particularly, they tested a single 3rd IFC value and found that the 3rd IFC decreases with increasing magnitude of the displacement used in FDM. Based on the test, they concluded that LDA converges at 0.03 Å while PBE at 0.07 Å.

However, all those studies have primarily focused on three-phonon scattering while the impact of different XC functionals on higher-order IFCs or scattering rates remains unclear, even though four-phonon scattering has been shown to be substantial even at room temperature.^{5,6,21} Furthermore, most studies focused on the effect of different XC functionals rather than the energy surface roughness of those XC functionals. In this paper, we investigate the impact of energy surface roughness of XC functionals on higher-order IFCs and thermal conductivity calculations. Crystalline Si is chosen as a benchmark material, BAs is picked for its representativity in higher-order phonon scattering, and NaCl is selected representing for low thermal conductivity materials. To test the energy surface roughness, we extract the 2nd-, 3rd-, and 4th-IFCs using a commonly used small displacement (δ , 0.01 Å, by default of Phonopy,²² Thirddorder,²³ and Fourthorder²⁴ packages) and a relatively large δ (0.03 Å) in the FDM for LDA, PBE, and PBEsol XC functionals (for NaCl, only PBE and PBEsol are considered). The thermal conductivity values and scattering rates are calculated by BTE and compared with each other.

Throughout the work, the DFT calculations are conducted by using the Vienna *ab initio* simulation package (VASP)²⁵ with the PAW²⁶ method and a plane wave energy cutoff of 500 eV. The lattice constant is relaxed with a $16 \times 16 \times 16$ k-mesh, electron energy convergence threshold of 10^{-8} eV, and force convergence threshold of 10^{-7} eV/Å. After relaxation, a $4 \times 4 \times 4$ (128 atoms) supercell with a $4 \times 4 \times 4$ k-mesh is used for the calculation of 2nd-, 3rd-, and 4th-IFCs using the Phonopy,²⁷ Thirddorder,²³ and Fourthorder²⁴ packages,

respectively. The 3rd- and 4th-IFCs calculations include up to the 6th and 2nd nearest neighbor atoms, respectively. Other settings are the same as relaxation. The thermal conductivity is calculated by the FourPhonon package,²⁴ a revised version of ShengBTE,²³ using a $16 \times 16 \times 16$ phonon $\mathbf{q}$ -mesh in an iterative manner. The broadening factor is set to 0.1. Natural isotope-phonon scattering is included.

The results for Si are shown in Fig. 1. The relaxed lattice constants by using LDA, PBE, and PBEsol XC functionals are 5.40, 5.47, and 5.44 Å, respectively, comparable to the experimental value of 5.43 Å.²⁸ This is also in line with the perception that LDA underestimates, PBE overestimates, and PBEsol well produces the lattice constants for crystals in general.^{15,29} The 2nd-, 3rd-, and 4th-IFCs of Si obtained using FDM with δ values of 0.01 and 0.03 Å for LDA, PBE, and PBEsol XC functionals are shown in Figs. 1(a)–1(c). We find that the 2nd- and 3rd-IFCs are not sensitive to the finite displacement (δ) for all the three XC functionals. This indicates that the energy surface is smooth to the 2nd- and 3rd-order derivatives for all the three XC functionals. As a result, the phonon dispersion does not change with δ , as shown in Fig. 1(d). In contrast, the 4th-IFCs are strongly sensitive to the δ . The results by using $\delta = 0.01$ Å and $\delta = 0.03$ Å are dramatically different from each other. Small δ produces larger 4th-IFCs. We also find that 4th-IFCs decrease with increasing δ and converge at 0.02 Å (see supplementary material, Fig. S1). This indicates that the fourth-order energy surface is not smooth and that a displacement of greater than 0.02 Å is needed to overcome the roughness.

To examine the impact on thermal conductivity predictions, for clarity, we compare values at 300 K without loss of generality as shown in Figs. 1(e) and 1(f). For all functionals, it is seen that the three-phonon thermal conductivity does not change significantly upon δ values. However, the thermal conductivity that includes four-phonon scattering changes significantly with δ values. With $\delta = 0.01$ Å, the predicted thermal conductivity is only ~20, ~60, and ~90 W/mK at room temperature using LDA, PBE, and PBEsol, respectively. These values are unphysically wrong, compared to experimental data of 130–150 W/mK.^{30–32} In contrast, with $\delta = 0.03$ Å, the thermal conductivity is predicted consistently among three different XC functionals at 110–120 W/mK, much closer to the experimental data. Although this value is slightly smaller than experimental data, it originates from the underestimation of the three-phonon thermal conductivity (as also seen in the work by Jain and McGaughey¹⁷) rather than four-phonon scattering. To match exactly with experimental thermal conductivity, other factors are needed, such as finite temperature corrections to all orders of IFCs and the $\mathbf{q}$ -mesh convergence, which are not the focus of this work. Moreover, the importance of four-phonon scattering relative to the three-phonon scattering at room temperature is predicted unphysically large when using $\delta = 0.01$ Å. This problem is solved after using $\delta = 0.03$ Å, and the predicted relative importance of four-phonon scattering is consistently about 5%–10% for all three XC functionals. This demonstrates the importance δ in 4th-IFCs and three+four-phonon thermal conductivity calculations. We further examine the effect of δ on three-phonon and four-phonon scattering rates. As shown in Figs. 1(g) and 1(h), for all XC functionals, three-phonon scattering rates can be predicted well even with a small δ , while four-phonon scattering rates are predicted unphysically wrong when using a small δ .

As a representative material in higher-order phonon scattering studies, BAs is selected to examine the sensitivity of IFCs and thermal

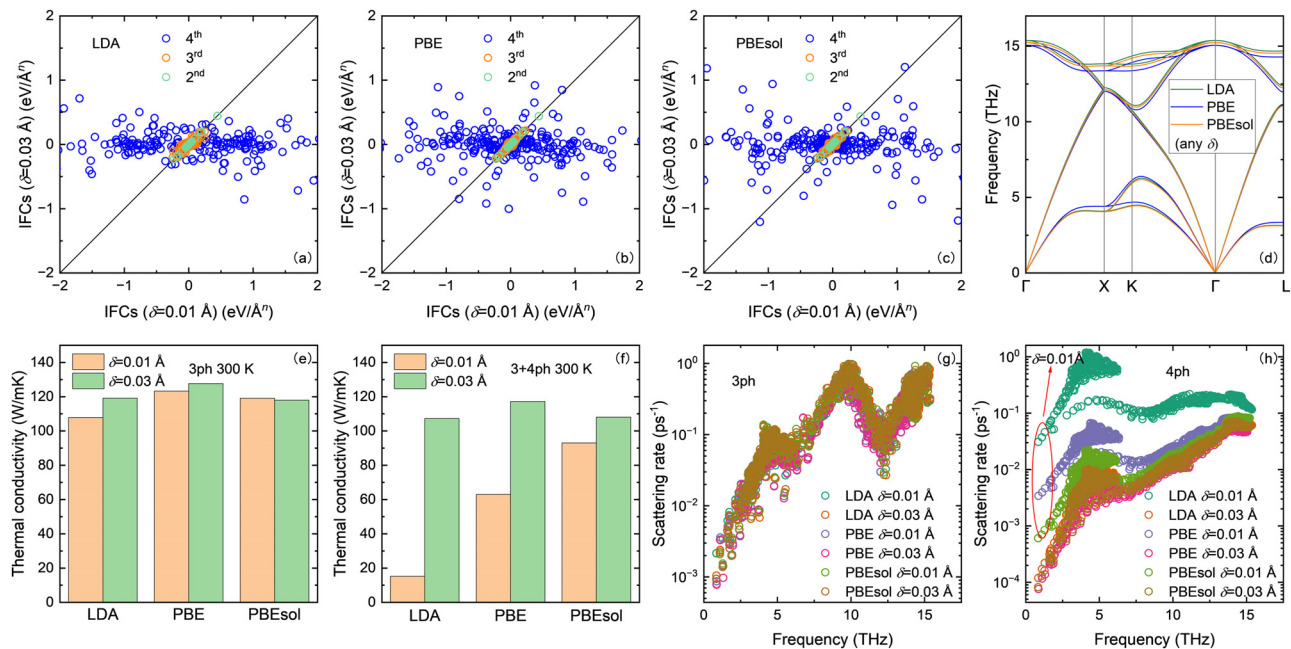


FIG. 1. The results for silicon. (a) The comparison of 2nd-, 3rd-, and 4th-IFCs calculated by using finite difference method with δ of 0.01 and 0.03 $\text{\AA}$ using the LDA functional. δ is the atomic displacement in the finite difference method. The superscript n of $\text{\AA}$ corresponds to the n th-order IFCs. (b) and (c) Same as (a) but use the PBE and PBEsol functionals, respectively. (d) Phonon dispersion using LDA, PBE, and PBEsol XC functionals calculated by using any δ from 0.01 to 0.03 $\text{\AA}$. (e) The comparison of three-phonon room-temperature thermal conductivity using LDA, PBE, and PBEsol XC functionals with δ of 0.01 and 0.03 $\text{\AA}$. (f) Same as (e) but includes four-phonon scattering in the thermal conductivity calculation. (g) and (h) Three and four-phonon scattering rates calculated with the force constants obtained by using different δ with LDA, PBE, PBEsol XC functionals.

conductivity to finite δ . As shown in Figs. 2(a)–2(c), for all the three XC functionals, the 2nd- and 3rd-IFCs are not sensitive to δ but the 4th-IFCs are. This sensitivity is exceptionally strong for the PBEsol functional. We further calculate 4th-IFCs using PBEsol with δ value of 0.02 $\text{\AA}$ as shown in Fig. 2(d). The converge criterion of δ is found to be the same as Si (see supplementary material, Fig. S2). Note that Figs. 2(a)–2(c) only show 4th-IFCs values inside the range of -2 to $2 \text{ eV}/\text{\AA}^4$ since only they are sensitive to δ . This is different from Si, in which all the 4th-IFCs values are sensitive to δ , but the values between -2 and $2 \text{ eV}/\text{\AA}^4$ account for a large portion, i.e., more than 93%, of the 4th-IFCs values in the 4th-IFCs matrix. These small 4th-IFCs significantly impact thermal conductivity calculations.

As shown in Fig. 2(e), the thermal conductivity that includes four-phonon scattering using PBEsol is significantly underestimated (i.e., by 40%) when using $\delta = 0.01 \text{ \AA}$. The room temperature value is only 765 W/mK, while LDA and PBE yield 1237 and 1164 W/mK, respectively, consistent with literature data.^{33–35} When a larger δ of 0.03 $\text{\AA}$ is used, the predicted thermal conductivity using PBEsol is improved significantly to 1171 W/mK, in agreement with LDA and PBE results. The discrepancy of three+four-phonon thermal conductivity in BAs using PBEsol with different δ is notable, which demonstrates that the small 4th-IFCs values between -2 and $2 \text{ eV}/\text{\AA}^4$ indeed significantly affect thermal conductivity calculations. We regard this as an important finding since PBEsol is generally believed to be the best and is gradually accepted as the default XC functionals when studying solid materials. Considering the fact that 0.01 $\text{\AA}$ is the default setting in Fourthorder script,²⁴ which is one of the most widely used scripts to

extract 4th-IFCs, the energy surface roughness issue could be one potential reason that researchers cannot reproduce the reasonable three+four-phonon thermal conductivity of BAs using PBEsol functional.

Three- and four-phonon scattering rates of BAs are shown in Figs. 2(f) and 2(g). Three-phonon scattering rates are consistent among different XC functionals for different δ values. Four-phonon scattering rates, especially those for acoustic phonons, are significantly overestimated when using PBEsol with $\delta = 0.01 \text{ \AA}$, leading to the large underestimation of thermal conductivity. As discussed previously, the dominant 4th-IFCs do not differ significantly, indicating that higher-order phonon scattering is sensitive to those relatively small IFCs. This is understandable since they occupy a large portion of elements in the IFC matrix.

For NaCl, a similar trend as silicon is observed, as shown in Fig. 3. Neither the 2nd- or 3rd-IFCs are sensitive to δ for PBE and PBEsol XC functionals, but the 4th-IFCs are extremely sensitive. The room-temperature three+four-phonon thermal conductivity predicted by the IFCs obtained using $\delta = 0.01 \text{ \AA}$ is around 1 W/mK, which is much lower than the experimental data ($\sim 6.5 \text{ W/mK}$).^{36,37} After increasing the δ value to 0.03 $\text{\AA}$, the thermal conductivity increases to around 5 W/mK, similar to literature calculations.³⁸ Though this value is still slightly lower than experimental data, it is shown in the literature that the underprediction can be resolved by considering finite-temperature phonon renormalization.^{38,39} Therefore, we have demonstrated the sensitivity of higher-order IFCs to the energy surface roughness for both high and low thermal conductivity materials.

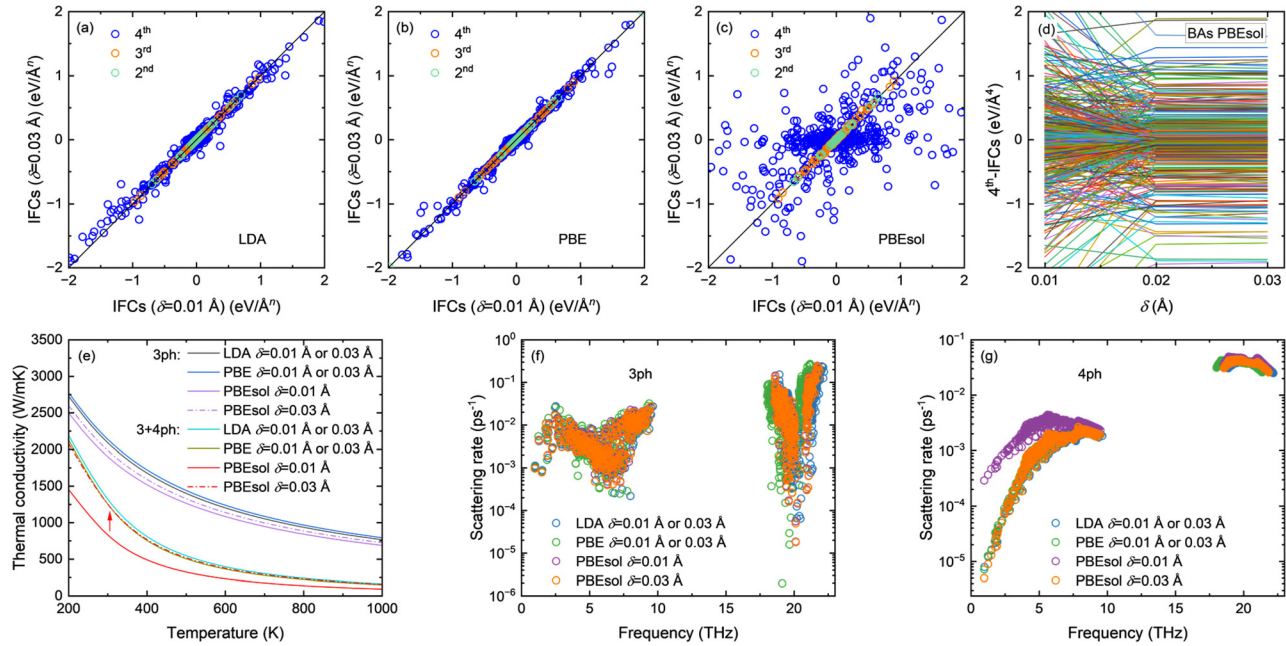


FIG. 2. The results for BAs. (a)–(c) The comparison of 2nd-, 3rd-, and 4th-IFCs of BAs calculated by using FDM with δ being 0.01 and 0.03 Å for (a) LDA, (b) PBE, and (c) PBEsol XC functionals. (d) The convergence test of δ for 4th-IFCs of BAs using PBEsol XC functional. (e) Temperature-dependent thermal conductivity of BAs using LDA, PBE, and PBEsol XC functionals with $\delta = 0.01$ and 0.03 Å. (f) and (g) Three- and four-phonon scattering rates calculated with the force constants obtained by using different δ with LDA, PBE, and PBEsol XC functionals.

After confirming the impact of δ in the higher-order IFCs calculations, a natural question is: What δ value should be used for general materials? The δ value cannot be too small that it includes the unphysical local roughness of potential energy surface or too large that it wipes out the curvature of the energy surface or exceeds the temperature of interest. To determine what δ values can be used for a certain temperature, we have calculated the average displacement of atoms along one Cartesian direction in Si, BAs, and NaCl as a function of temperature by using TDEP,⁴⁰ as shown in Fig. 4. In this work, we are only interested

in 0 K force constants. Based on Fig. 4, δ can be taken up to about 0.03, 0.035, and 0.045 Å for BAs, Si, and NaCl, respectively. A safe range would be 0.03–0.04 Å. For finite temperature IFCs calculations, an appropriately larger δ should be used, but it needs further investigation. Note that the $\delta = 0.03$ Å used in this work is still below the average displacement at 100 K, indicating that the difference between $\delta = 0.01$ and 0.03 Å in Si, BAs, and NaCl found in this work is not a result of temperature effect. This can be also seen from the fact that 3rd-IFCs and three-phonon thermal conductivity are not sensitive to $\delta < 0.03$ Å.

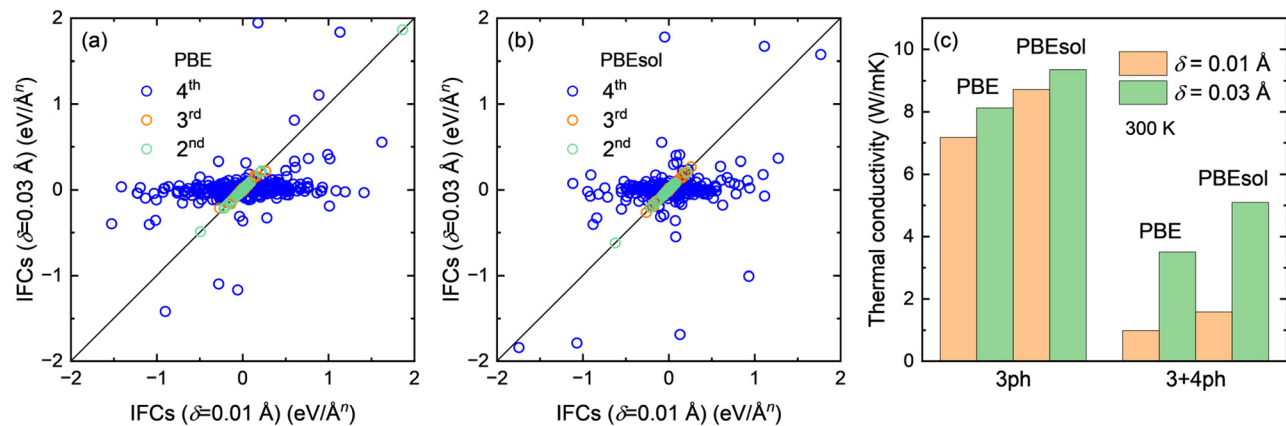


FIG. 3. The results for NaCl. (a) and (b) The comparison of 2nd-, 3rd-, and 4th-IFCs calculated by using FDM with $\delta = 0.01$ and 0.03 Å for (a) PBE and (b) PBEsol XC functionals. (c) Three-phonon and three+four-phonon room-temperature thermal conductivities using PBE and PBEsol XC functionals with $\delta = 0.01$ and 0.03 Å.

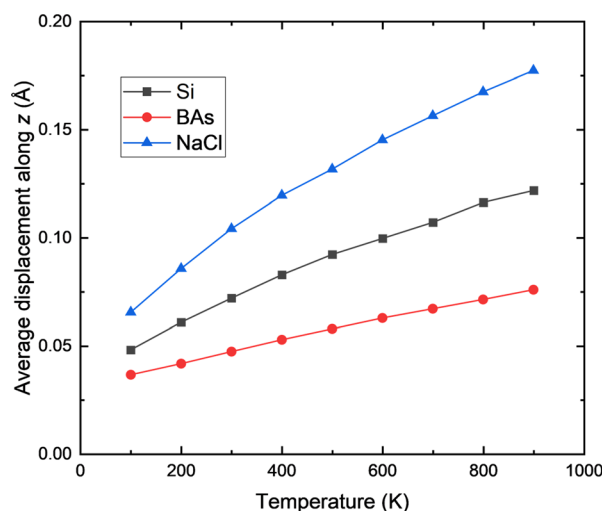


FIG. 4. Temperature-dependent average atomic displacement along the z axis in Si, BAs, and NaCl.

In conclusion, we find that the 4th-IFCs are very sensitive to the energy surface roughness of XC functionals, while 2nd- and 3rd-IFCs are not. A large enough finite displacement in the FDM calculations is needed to overcome the energy surface roughness to the 4th order. Taking Si, BAs, and NaCl as examples, we find that the atomic displacement of at least $0.02 \text{ \AA}$ is needed to correctly predict 4th-IFCs. For Si, when using a small displacement ($\delta = 0.01 \text{ \AA}$), the three+four-phonon thermal conductivity can be underestimated by as much as 80% when using different XC functionals. For BAs, the three+four-phonon thermal conductivity is underestimated by 40% when using PBEsol and $\delta = 0.01 \text{ \AA}$. For NaCl, the three+four-phonon thermal conductivity is underestimated by 70% with $\delta = 0.01 \text{ \AA}$. The sensitivity of 4th-IFCs and four-phonon scattering is both material and XC functional dependent. A safe range of δ would be $0.03\text{--}0.04 \text{ \AA}$ to overcome the energy surface roughness but not to wipe out the curvature of the energy surface or exceed the temperature of interest. We expect that this work will provide valuable guidance for future phonon scattering and thermal transport study.

See the supplementary material for the additional convergence tests for the impact of δ in the calculation of IFCs for Si and BAs.

This work was supported through the INL Laboratory Directed Research and Development (LDRD) Program under DOE Idaho Operations Office Contract No. DE-AC07-05ID14517, LDRD Project ID 23A1070-064FP. H.Z. and T.F. also acknowledge the support from the National Science Foundation (NSF) (Award No. CBET 2212830). The computation used Center for High Performance Computing (CHPC) at the University of Utah, Bridges-2 at Pittsburgh Supercomputing Center through allocation PHY220002 from the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) program, which is supported by NSF Grant Nos. 2138259, 2138286, 2138307, 2137603, and 2138296, and Idaho National Laboratory's High Performance Computing systems located at the Collaborative Computing Center

and supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities under Contract No. DE-AC07-05ID14517.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Hao Zhou: Data curation (lead); Formal analysis (lead); Writing – original draft (lead). **Shuxiang Zhou:** Conceptualization (supporting); Formal analysis (supporting); Funding acquisition (equal); Writing – review & editing (supporting). **Zilong Hua:** Conceptualization (supporting); Formal analysis (supporting); Funding acquisition (supporting); Writing – review & editing (supporting). **Kaustubh Bawane:** Conceptualization (supporting); Formal analysis (supporting); Investigation (supporting); Writing – review & editing (supporting). **Tianli Feng:** Conceptualization (lead); Formal analysis (supporting); Funding acquisition (equal); Investigation (supporting); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material. Additional data are available from the corresponding authors upon reasonable request.

REFERENCES

- A. L. Moore and L. Shi, "Emerging challenges and materials for thermal management of electronics," *Mater. Today* **17**(4), 163–174 (2014).
- D. R. Clarke, M. Oechsner, and N. P. Padture, "Thermal-barrier coatings for more efficient gas-turbine engines," *MRS Bull.* **37**(10), 891–898 (2012).
- G. J. Snyder and E. S. Toberer, *Materials for Sustainable Energy* (Macmillan Publishers Ltd, UK, 2010), pp. 101–110.
- D. A. Broido, M. Malorny, G. Birner, N. Mingo, and D. A. Stewart, "Intrinsic lattice thermal conductivity of semiconductors from first principles," *Appl. Phys. Lett.* **91**(23), 231922 (2007).
- T. Feng and X. Ruan, "Quantum mechanical prediction of four-phonon scattering rates and reduced thermal conductivity of solids," *Phys. Rev. B* **93**(4), 045202 (2016).
- T. Feng, L. Lindsay, and X. Ruan, "Four-phonon scattering significantly reduces intrinsic thermal conductivity of solids," *Phys. Rev. B* **96**(16), 161201 (2017).
- L. Lindsay, C. Hua, X. L. Ruan, and S. Lee, "Survey of *ab initio* phonon thermal transport," *Mater. Today Phys.* **7**, 106–120 (2018).
- T. Feng and X. Ruan, *Nanoscale Energy Transport* (IOP Publishing, 2020), pp. 2–1–2–44.
- G. Kresse, J. Furthmüller, and J. Hafner, "Ab initio force constant approach to phonon dispersion relations of diamond and graphite," *Europhys. Lett. (EPL)* **32**(9), 729–734 (1995).
- W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.* **140**, A1133 (1965).
- R. G. Parr, S. R. Gadre, and L. J. Bartolotti, "Local density functional theory of atoms and molecules," *Proceedings of the National Academy of Sciences* **76**(6), 2522–2526 (1979).
- A. Taheri, C. Da Silva, and C. H. Amon, "First-principles phonon thermal transport in graphene: Effects of exchange-correlation and type of pseudopotential," *J. Appl. Phys.* **123**(21), 215105 (2018).
- J. P. Perdew and A. Zunger, "Self-interaction correction to density-functional approximations for many-electron systems," *Phys. Rev. B* **23**(10), 5048–5079 (1981).

- ¹⁴J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.* **77**(18), 3865–3868 (1996).
- ¹⁵J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, "Restoring the density-gradient expansion for exchange in solids and surfaces," *Phys. Rev. Lett.* **100**(13), 136406 (2008).
- ¹⁶J. P. Perdew and Y. Wang, "Erratum: Accurate and simple analytic representation of the electron-gas correlation energy [Phys. Rev. B **45**, 13244 (1992)]," *Phys. Rev. B* **98**(7), 079904 (2018).
- ¹⁷A. Jain and A. J. H. McGaughey, "Effect of exchange-correlation on first-principles-driven lattice thermal conductivity predictions of crystalline silicon," *Comput. Mater. Sci.* **110**, 115–120 (2015).
- ¹⁸G. Qin, Z. Qin, H. Wang, and M. Hu, "On the diversity in the thermal transport properties of graphene: A first-principles-benchmark study testing different exchange-correlation functionals," *Comput. Mater. Sci.* **151**(May), 153–159 (2018).
- ¹⁹B. Mortazavi, E. V. Podryabinkin, I. S. Novikov, T. Rabczuk, X. Zhuang, and A. V. Shapeev, "Accelerating first-principles estimation of thermal conductivity by machine-learning interatomic potentials: A MTP/ShengBTE solution," *Comput. Phys. Commun.* **258**, 107583 (2021).
- ²⁰B. Dongre, J. Carrete, N. Mingo, and G. K. H. Madsen, "Thermal conductivity of group-III phosphides: The special case of GaP," *Phys. Rev. B* **106**(20), 205202 (2022).
- ²¹X. Yang, T. Feng, J. Li, and X. Ruan, "Stronger role of four-phonon scattering than three-phonon scattering in thermal conductivity of III-V semiconductors at room temperature," *Phys. Rev. B* **100**(24), 245203 (2019).
- ²²A. Togo and I. Tanaka, "First principles phonon calculations in materials science," *Scr. Mater.* **108**, 1–5 (2015).
- ²³W. Li, J. Carrete, N. A. Katcho, and N. Mingo, "ShengBTE: A solver of the Boltzmann transport equation for phonons," *Comput. Phys. Commun.* **185**(6), 1747–1758 (2014).
- ²⁴Z. Han, X. Yang, W. Li, T. Feng, and X. Ruan, "FourPhonon: An extension module to ShengBTE for computing four-phonon scattering rates and thermal conductivity," *Comput. Phys. Commun.* **270**, 108179 (2022).
- ²⁵G. Kresse and J. Furthmüller, "Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set," *Phys. Rev. B* **54**(16), 11169–11186 (1996).
- ²⁶P. E. Blöchl, "Projector augmented-wave method," *Phys. Rev. B* **50**(24), 17953–17979 (1994).
- ²⁷A. Togo, F. Oba, and I. Tanaka, "First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂," *Phys. Rev. B* **78**(13), 134106 (2008).
- ²⁸Y. Okada and Y. Tokumaru, "Precise determination of lattice parameter and thermal expansion coefficient of silicon between 300 and 1500 K," *J. Appl. Phys.* **56**(2), 314–320 (1984).
- ²⁹G. I. Csonka, J. P. Perdew, A. Ruzsinszky, P. H. T. Philipsen, S. Lebègue, J. Paier, O. A. Vydrov, and J. G. Ángyán, "Assessing the performance of recent density functionals for bulk solids," *Phys. Rev. B* **79**(15), 155107 (2009).
- ³⁰H. R. Shanks, P. D. Maycock, P. H. Sidles, and G. C. Danielson, "Thermal conductivity of silicon from 300 to 1400°K," *Phys. Rev.* **130**(5), 1743–1748 (1963).
- ³¹C. J. Glassbrenner and G. A. Slack, "Thermal conductivity of silicon and germanium from 3°K to the melting point," *Phys. Rev.* **134**(4A), A1058–A1069 (1964).
- ³²A. V. Inyushkin, A. N. Taldenkov, A. M. Gibin, A. V. Gusev, and H. -J. Pohl, "On the isotope effect in thermal conductivity of silicon," *Phys. Status Solidi C* **1**(11), 2995–2998 (2004).
- ³³J. S. Kang, M. Li, H. Wu, H. Nguyen, and Y. Hu, "Experimental observation of high thermal conductivity in boron arsenide," *Science* **361**(6402), 575–578 (2018).
- ³⁴S. Li, Q. Zheng, Y. Lv, X. Liu, X. Wang, P. Y. Huang, D. G. Cahill, and B. Lv, "High thermal conductivity in cubic boron arsenide crystals," *Science* **361**(6402), 579–581 (2018).
- ³⁵F. Tian, B. Song, X. Chen, N. K. Ravichandran, Y. Lv, K. Chen, S. Sullivan, J. Kim, Y. Zhou, T. H. Liu, M. Goni, Z. Ding, J. Sun, G. A. G. U. Gamage, H. Sun, H. Ziyade, S. Huyan, L. Deng, J. Zhou, A. J. Schmidt, S. Chen, C. W. Chu, P. Y. Huang, D. Broido, L. Shi, G. Chen, and Z. Ren, "Unusual high thermal conductivity in boron arsenide bulk crystals," *Science* **361**(6402), 582–585 (2018).
- ³⁶K. A. McCarthy and S. S. Ballard, "Thermal conductivity of eight halide crystals in the temperature range 220°K to 390°K," *J. Appl. Phys.* **31**(8), 1410–1412 (1960).
- ³⁷H. Yukutake and M. Shimada, "Thermal conductivity of NaCl, MgO, coesite and stishovite up to 40 kbar," *Phys. Earth Planet. Inter.* **17**(3), 193–200 (1978).
- ³⁸N. K. Ravichandran and D. Broido, "Unified first-principles theory of thermal properties of insulators," *Phys. Rev. B* **98**(8), 085205 (2018).
- ³⁹Y. Xia, V. I. Hegde, K. Pal, X. Hua, D. Gaines, S. Patel, J. He, M. Aykol, and C. Wolverton, "High-throughput study of lattice thermal conductivity in binary rocksalt and zinc blende compounds including higher-order anharmonicity," *Phys. Rev. X* **10**(4), 041029 (2020).
- ⁴⁰O. Hellman, I. A. Abrikosov, and S. I. Simak, "Lattice dynamics of anharmonic solids from first principles," *Phys. Rev. B* **84**(18), 180301 (2011).