

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

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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.

Keywords: exchange-correlation functionals, density functional theories, first principles, thermal conductivity, fourth-order force constants, four-phonon scattering

Accurately predicting lattice thermal conductivity holds immense significance in a wide range of applications such as thermal management¹, thermal barrier coatings², and thermoelectric devices³. 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 prediction⁴⁻⁸. 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 10 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 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 found that the effect of XC functionals on thermal conductivity is negligible.¹⁹ Dongre *et al.* found 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 Phonopy²², Thirdorder²³, and Fourthorder²⁴ packages) and a relatively large δ (0.03 Å²⁰) 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 via BTE and compared.

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 Phonopy²⁷, Thirddorder²³, and Fourthorder²⁴ packages, respectively. The 3rd- and 4th-IFCs calculation 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 package²⁴, a revised version of ShengBTE²³, using a $16 \times 16 \times 16$ phonon **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 Å²⁸. 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 Å and 0.03 Å for LDA, PBE, and PBEsol XC functionals are shown in Figs. 1 (a-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 , and the results are shown in Fig. 1 (d) for different XC functionals. In contrast, the 4th-IFCs is 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 converges at 0.02 Å (See

supplemental 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.

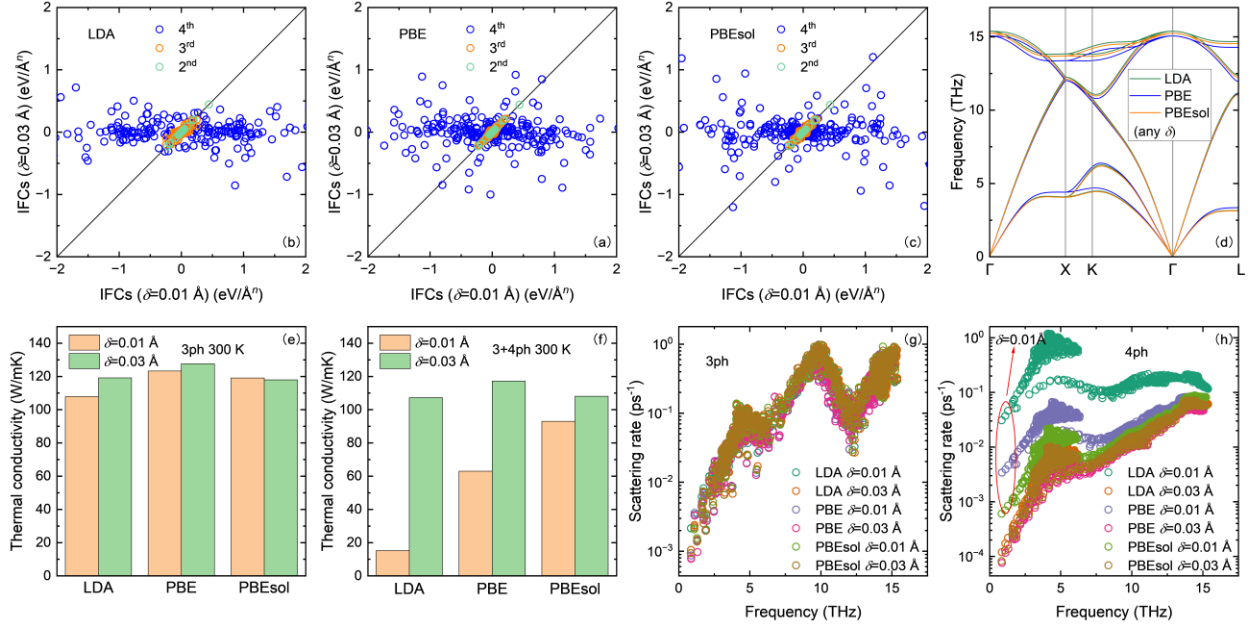


FIG. 1. The results for silicon. (a) The comparison of 2nd-, 3rd- and 4th-IFCs calculated by using finite difference method with δ of 0.01 Å and 0.03 Å using the LDA exchange-correlation functional. δ is the atomic displacement in the finite difference method. The superscription n of Å corresponds to the n^{th} -order IFCs. (b,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 Å. (e) The comparison of three-phonon room temperature thermal conductivity using LDA, PBE, and PBEsol XC functionals with δ of 0.01 Å and 0.03 Å. (f) Same as (e) but includes four-phonon scattering in the thermal conductivity calculation. (g,h) Three and four-phonon scattering rates calculate with the force constants obtained by using different δ with LDA, PBE, PBEsol XC functionals.

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,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/mK³⁰⁻³². 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 needs other factors such as finite temperature corrections to all orders of IFCs and the q-mesh convergence, which is 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,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 .

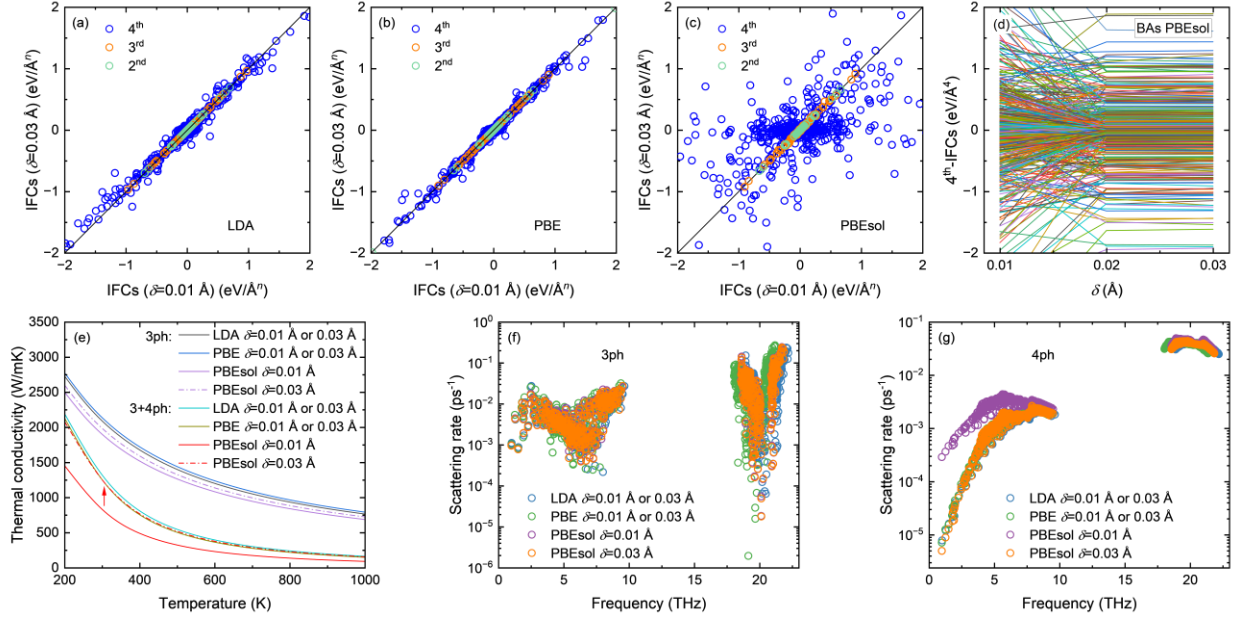


FIG. 2. The results for BAs. (a,b,c) The comparison of 2nd-, 3rd- and 4th-IFCs of BAs calculated by using FDM with δ being 0.01 Å and 0.03 Å for (a) LDA, (b) PBE and (c) PBEsol XC functionals. (d) The convergence test of δ for 4th-IFCs of BAs using PBEsol XC functional. (e) Temperature-dependent thermal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

As a representative material in higher-order phonon scattering, the sensitivity of IFCs and thermal conductivity of BAs to finite δ is examined. As shown in Figs. 2 (a-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 Å as shown in Fig. 2 (d). The converge criterion of δ is found to be the same as Si, 0.02 Å (see supplemental Fig. S2.). Note that Figs. 2 (a-c) only shows 4th-IFCs values inside the range of -2 to 2 eV/Å^4 since only the 4th-IFCs values in this range are sensitive to δ , while the values greater than 2 eV/Å^4 or smaller than -2 eV/Å^4 are not sensitive to δ . This is different from Si, in which all the 4th-IFCs values are sensitive to δ , but the values between -2 to 2 eV/Å^4 account for a large portion, i.e., more than 93%, of the 4th-IFCs values in the 4th-IFCs matrix. Further

calculations of thermal conductivity will demonstrate the sensitivity of the 4th-IFCs has strong impact.

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 $\delta=0.01$ Å. 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 Å 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 eV/Å⁴ 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 Å is the default setting in Fourthorder script²⁴, which is one of the most famous scripts to generate supercells with finite displacements 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 are shown in Figs. 2 (f,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 $\delta=0.01$ Å, 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 higher-order derivative should be more sensitive to the digital precision.

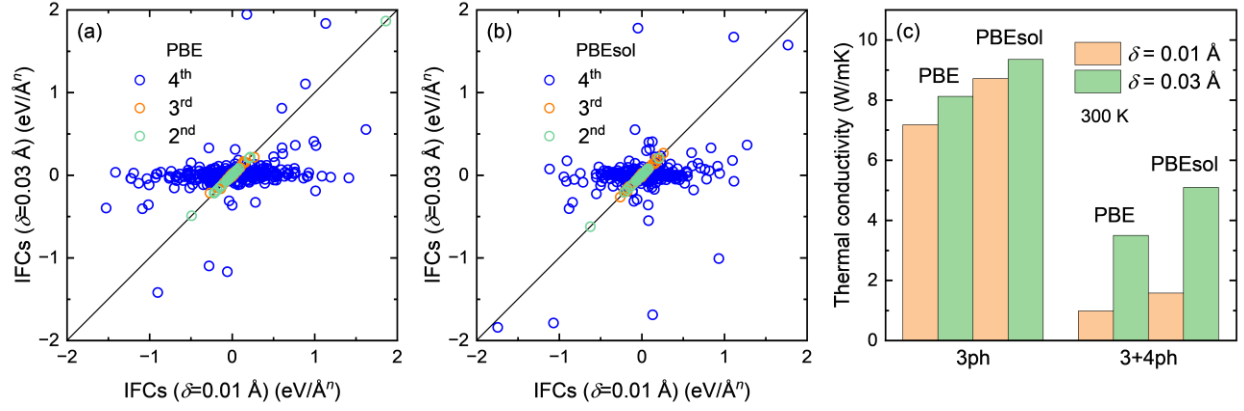


FIG. 3. The results for NaCl. (a,b) The comparison of 2nd-, 3rd- and 4th-IFCs calculated by using FDM with $\delta = 0.01$ Å and 0.03 Å for (a) PBE and (b) PBEsol XC functionals. (c) Three-phonon and three+four-phonon room temperature thermal conductivity using PBE and PBEsol XC functionals with $\delta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

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 $\delta = 0.01$ Å is around 1 W/mK, which is much lower than the experimental data (~ 6.5 W/mK)^{36,37}. After increasing the δ value to 0.03 Å, the thermal conductivity increases to around 5 W/mK, similar to literature calculations³⁸. Though this value is still slightly lower than experimental data, it is shown in literature that the underprediction is mainly due to the finite-temperature correction to the ground state calculation^{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.

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 to include the

unphysical local roughness of potential energy surface or too large to wipe out the curvature of the energy surface or exceed the temperature of interest. The δ value cannot be too large to exceed 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 obtained by TDEP⁴⁰, 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.

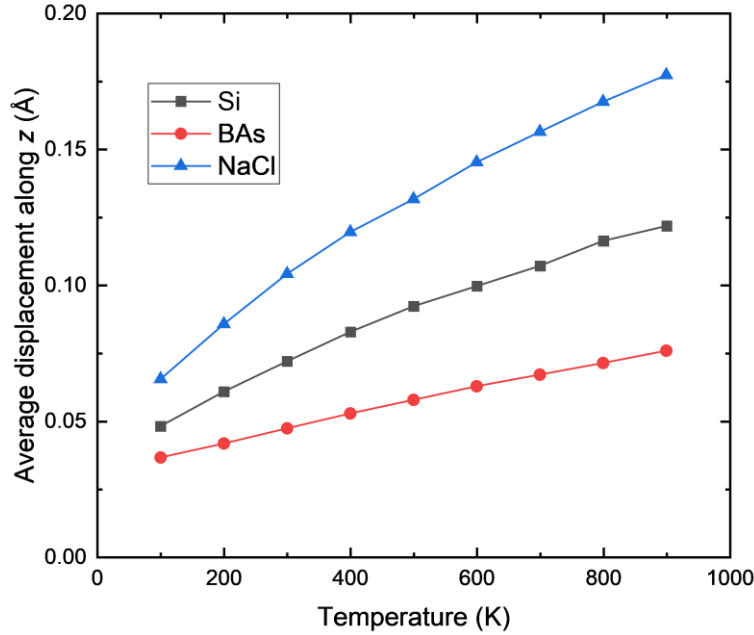


FIG. 4. Temperature-dependent average atomic displacement along the z axis in Si, BAs and NaCl.

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 IFCs 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 Å 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 0.03-0.04 Å 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 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.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author contributions

T.F. conceived the idea. T.F. and S.Z. guided the project. H.Z. performed the simulations and wrote the original manuscript. T.F. revised the manuscript. H.Z., S.Z., Z.H., K.B., and T.F. all participated in the discussion and approved the manuscript.

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.

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