Wang Lipeng_{Application} of First-Principles to Thermal Neutron Scattering Cross-Section Calculations

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Date: 2023-06-20T00:00:00+00:00

Abstract

First-principles methods have been applied to calculate thermal neutron cross-sections for thermal neutron scattering materials relevant to nuclear engineering. Using the generation of thermal neutron cross-sections for Al and Bi metals as examples, this study calculates their phonon dispersion relations and phonon density of states using VASP combined with the PHONONY program, based on both the first-principles frozen phonon method and density functional perturbation theory. Employing the NJOY program, Bi coherent scattering treatment is incorporated in LEAPR to generate thermal neutron scattering cross-section libraries for Al and Bi. The results demonstrate that for Al, the thermal neutron scattering cross-section derived from the phonon density of states using density functional perturbation theory shows better agreement with ENDF/B-VIII.0 than that from the frozen phonon method. For Bi, the density functional perturbation method eliminates the imaginary frequency phenomenon associated with the frozen phonon method, yielding thermal neutron scattering results that agree well with experimental values. This work proposes a more fundamental and predictive approach for generating thermal neutron cross-sections from the perspective of exploring internal characteristic mechanisms of materials, thereby establishing a theoretical foundation for investigating the thermalization mechanisms of nuclear materials in advanced reactors.

Full Text

Application of First-Principles Methods in Thermal Neutron Scattering Cross Section Calculations

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Abstract: First-principles methods have been applied to calculate thermal neutron scattering cross sections for materials of interest in nuclear engineering. Using Al and Bi metals as examples, this work employs both the frozen phonon method and density functional perturbation theory (DFPT) based on first-principles calculations. The phonon dispersion relations and phonon density of states (DOS) were computed using VASP combined with the PHONONPY program. Thermal neutron scattering cross-section libraries for Al and Bi were then generated using the NJOY program, with coherent scattering treatment for Bi added to the LEAPR module. The results demonstrate that for Al, the thermal neutron scattering cross sections derived from DFPT phonon DOS agree better with ENDF/B-VIII.0 than those from the frozen phonon method. For Bi, the DFPT method eliminates the imaginary frequency phenomenon observed in the frozen phonon approach, yielding thermal neutron scattering results that show good agreement with experimental values. This study proposes a more fundamental and predictive approach for generating thermal neutron cross sections from the perspective of exploring intrinsic material mechanisms, establishing a theoretical foundation for investigating the thermalization mechanisms of nuclear materials in advanced reactor designs.

Keywords: First-principles; Phonon density of states; Thermal neutron scattering cross section; Nuclear data generation

Introduction

Computer simulation tools are widely employed in reactor engineering. In recent years, advanced simulation and modeling techniques developed abroad, leveraging high-performance computing capabilities and "first-principles" physics-based models to replace empirical formulas, have enabled predictive simulation of complex systems in virtual environments. These approaches have achieved significant progress and benefits in materials research, climate prediction, and other fields. In nuclear science and technology research and engineering design, improved accuracy in nuclear design can be achieved through two avenues: enhancing computational models and methods, and improving the precision of nuclear data. For nuclear engineers, correctly understanding and utilizing nuclear data is crucial, as it forms the prerequisite and foundation for obtaining accurate computational results.

Thermal neutron scattering data for moderator materials are particularly critical for nuclear design and neutronics analysis in thermal reactors, as well as for thermal neutron filter and cold neutron source design. Thermal neutron scattering cross sections depend not only on neutron energy but also on the temperature, physical, and chemical properties of the scattering medium, reflecting the intrinsic phonon density of states characteristics of the material. Conventional phonon DOS for common moderator materials were mostly based on simplified phonon models from the 1960s, which required numerous approximations to

generate thermal neutron scattering data and introduced significant errors in reactor criticality and neutron spectrum calculations. Over the past decade, researchers have investigated various methods for generating thermal neutron scattering data based on first-principles and molecular dynamics theories, continuously updating international nuclear evaluation databases. Early ENDF/B-VI.8 contained only fifteen thermal neutron scattering materials, ENDF/B-VII.0 had twenty, ENDF/B-VII.1 expanded to twenty-one, and the latest ENDF/B-VIII.0 provides thirty-four thermal scattering data entries for twenty-four thermalized materials. The database now effectively handles different structures of the same material—for instance, three thermal scattering datasets for graphite with different porosities are provided. Most of these expanded thermal neutron scattering libraries were completed using phonon DOS obtained from first-principles and molecular dynamics simulations.

Calculating phonon DOS for thermal neutron materials requires understanding the dynamics of atomic systems, including lattice structure and vibration modes represented by phonon dispersion relations and polarization vectors. These vibrations can be expressed as phonon DOS. Traditional phonon DOS calculations involved constructing analytical models of interatomic interactions, evaluating force constants, building dynamical matrices, and performing diagonalization. Force constants in dynamical matrix calculations could be estimated through various methods, generally derived from thermodynamic properties such as specific heat or compressibility data. Alternatively, phonon dispersion relations could be inferred from experimental measurements using inelastic scattering techniques. Both approaches essentially involve fitting semi-analytical relationships to experimental data, suffering from two major deficiencies: they are not predictive, as the derived atomic force constants and dispersion relations are extrapolated from experimental data, and the results are not unique, potentially being replaced by other dynamical models.

In contrast, first-principles methods are more physically fundamental, requiring no experimental data fitting. These methods treat multi-element atomic systems as many-particle systems composed of atomic nuclei and electrons. Based on quantum mechanical principles and without introducing any experimental parameters, they process multi-atomic systems for different lattice structures using rigorous and accurate density functional theory. The solid is abstracted as an ideal crystal with translational periodicity, with atoms assumed to oscillate around their equilibrium positions, reducing the problem to solving single-electron motion in a periodic potential. Compared to previous calculations relying on empirical formulas and simple dynamical models, first-principles calculations of material phonon DOS offer clear advantages in generality, enabling more complex and systematic multi-atomic dynamical models and establishing an important theoretical foundation for thermal neutron scattering cross-section calculations.

To meet the urgent demand for thermal neutron scattering data in thermal reactor design and address current challenges in thermal neutron scattering data gen-

eration and processing techniques, this study investigates first-principles-based thermal neutron scattering cross-section calculations. The paper is organized as follows: Section 1 provides a brief overview of thermal neutron scattering theory; Section 2 describes the first-principles calculation methods and modeling for Al and Bi metal thermal neutron scattering data; Section 3 presents and discusses the calculation results for Al and Bi thermal neutron scattering data.

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1 Thermal Neutron Scattering Theory

In thermal neutron reactors, for neutrons with energies below 1 eV, the neutron energy is comparable to the thermal energy of scattering nuclei, so target nuclei cannot be considered stationary. In this regime, neutrons readily undergo inelastic collisions with lattice ions, gaining or losing energy through phonon annihilation and creation, represented by thermal neutron inelastic scattering cross sections. Additionally, because the de Broglie wavelength of low-energy neutrons is similar to interatomic spacings in materials, interference may occur between neutrons scattered by different nuclei—the Bragg effect—represented by coherent elastic scattering cross sections. Thermal neutron scattering cross sections are thus not simply functions of neutron energy but also depend on the temperature and physical/chemical properties of the scattering medium, reflecting the material's phonon DOS characteristics. Therefore, investigating phonon vibration properties of scattering materials is essential.

For inelastic scattering cross sections, including coherent and incoherent components—which are important for all materials—the thermal scattering law is used. Inelastic scattering cross sections are generally derived from double-differential scattering cross sections:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{\sigma_b}{4\pi k_B T}\sqrt{\frac{E'}{E}}S_s(\alpha,\beta)$$

where E and E' are the incident and scattered neutron energies in the laboratory frame, Ω is the scattering angle in the laboratory frame, and T is the temperature in eV. To calculate inelastic scattering cross sections, the LEAPR and THERMR modules in the NJOY program are typically employed. NJOY calculations are primarily based on the "incoherent approximation," which assumes:

$$S(\alpha,\beta) = \frac{\sigma_{coh}}{\sigma_b}S_s(\alpha,\beta) + \frac{\sigma_{inc}}{\sigma_b}S_s(\alpha,\beta)$$

where σ_{coh} is the bound-atom coherent scattering cross section of the material, σ_{inc} is the bound-atom incoherent scattering cross section, α is the momentum transfer, and β is the energy transfer, expressed as:

$$\alpha = \frac{E' + E - 2\sqrt{EE'}\cos\theta}{Ak_BT}$$

$$\beta = \frac{E' - E}{k_BT}$$

$S_s(\alpha, \beta)$ is the self-scattering law without interactions, which can be written as:

$$S_s(\alpha, \beta) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\beta t}e^{-\alpha\gamma(t)}dt$$

where $\hat{t}$ is the measurement time in seconds, and $\hat{\gamma}(t)$ is expressed as:

$$\hat{\gamma}(t) = \int_0^{\infty} \frac{\rho(\omega)}{\omega}\left[\coth\left(\frac{\hbar\omega}{2k_BT}\right)[1-\cos(\omega t)] + i\sin(\omega t)\right]d\omega$$

The term $\rho(\omega)$ is the phonon DOS in units of barns, normalized such that $\int_0^{\infty}\rho(\omega)d\omega = 1$. This phonon DOS is the only external input required by NJOY and represents the key output from our first-principles calculations, directly influencing the quality and accuracy of thermal neutron scattering data.

When α and β values are large ($\alpha \geq 10$), corresponding to higher incident energies, they exceed the range of $S(\alpha, \beta)$. In this case, the short collision time (SCT) approximation must be introduced. The thermal neutron inelastic scattering expression under SCT is:

$$S_{SCT}(\alpha, \beta) = \frac{1}{\sqrt{4\pi\alpha T_{eff}}}\exp\left[-\frac{(\beta-\alpha)^2}{4\alpha T_{eff}}\right]$$

The resulting double-differential cross section under "short collision time" becomes:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{\sigma_b}{4\pi}\sqrt{\frac{E'}{E}}\frac{1}{\sqrt{4\pi\alpha T_{eff}}}\exp\left[-\frac{(\beta-\alpha)^2}{4\alpha T_{eff}}\right]$$

where the effective temperature is calculated from the phonon spectrum:

$$T_{eff} = \frac{1}{2k_B}\int_0^{\infty}\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)\rho(\omega)d\omega$$

For materials composed of coherent scatterers, the zero-phonon term gives the coherent scattering function, with the corresponding coherent scattering cross section:

$$\frac{d\sigma_{coh}}{d\Omega} = \frac{\sigma_{coh}}{4\pi} e^{-2W} \sum_{\tau} \delta(\mathbf{Q} - \ ) \frac{(2\pi)^3}{v_0}$$

where W is the Debye-Waller factor, $\mathbf{Q}$ is the momentum transfer vector, is the reciprocal lattice vector, and v_0 is the unit cell volume. The structure factor coefficient d_m is related to the lattice structure:

$$d_m = \frac{1}{N} \sum_i e^{i\ m \cdot \mathbf{r}_i}$$

where $F(t) = \sum_i e^{i\ m \cdot \mathbf{r}_i}$ is the phase per atom. Integrating equation (10) over angle and energy yields:

$$\sigma_{coh} = \sum_m d_m^2 e^{-2W_m} \delta(E' - E)$$

where $\tau_m = \sum_i \ell_i \mathbf{b}_i$ is the reciprocal lattice shell vector length, with ℓ_i as Miller indices and $\mathbf{b}_i$ as reciprocal basis vectors. Structure factor calculations differ for various crystal lattices. The LEAPR module in NJOY only includes built-in structures for face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP). For structures not matching these built-in options, users must input structure factors and recompile the LEAPR module. For example, Bi metal, which belongs to the rhombohedral system with two atoms per unit cell and a rhombohedral angle of 57.23°, requires special treatment. At 298.0 K, the Bi atomic position parameter is $z = 0.2271$, and reciprocal lattice shell vectors can be expressed as:

$$= \ell_1 \mathbf{b}_1 + \ell_2 \mathbf{b}_2 + \ell_3 \mathbf{b}_3$$

where $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are coordinate vectors expressed as:

$$\mathbf{b}_1 = \frac{2\pi}{a} \left(\hat{x} - \frac{1}{\sqrt{3}} \hat{y} + \frac{c}{a} \hat{z} \right)$$

with a and c as Bi lattice parameters in the corresponding hexagonal coordinate system. The unit cell contains two Bi atoms located at coordinates (Z, Z, Z) and $(-Z, -Z, -Z)$. From equation (12), the lattice structure factor for Bi can be derived as:

$$d_m = 2\cos[2\pi Z(\ell_1 + \ell_2 + \ell_3)]$$

2 Calculation Methods and Modeling

This study first investigated first-principles methods for generating phonon DOS, which can be divided into two categories. The first is the direct method, which calculates displacement amplitude functions based on energy differences between distorted and ideal lattices, then derives the force constant matrix by displacing atoms to compute phonon DOS—known as the frozen phonon method. The second is the indirect method, which obtains phonon DOS by describing the response of valence electron density to perturbations in the periodic lattice—called density functional perturbation theory (DFPT). Common software includes CASTEP, VASP, PHONON, and PHONONPY. VASP combined with the commercial PHONON code uses the frozen phonon (FP) direct method, while CASTEP employs the DFPT method. This work utilizes the VASP program combined with the open-source PHONONPY package, which can implement both FP and DFPT methods through scripting.

[Figure 1: see original paper] illustrates the workflow for calculating phonon DOS using the first-principles frozen phonon method. The process begins by selecting the unit cell to calculate and generating its supercell structure. Atoms are displaced symmetrically to compute forces on all atoms, constructing the force constant matrix. Fourier transformation of the force constant matrix yields the dynamical matrix, which is then diagonalized to compute the material's phonon dispersion curves. Analysis of these dispersion relations provides the phonon DOS, which can then be used to generate thermal neutron scattering data and related thermodynamic properties. This direct method, based on total energy changes or forces from atomic displacements from equilibrium positions, can produce phonon DOS as long as atomic forces are derivable. However, its drawback is the requirement for supercells, making it less suitable for simple crystal structures with small inter-unit-cell interactions. DFPT, as an indirect method, is an analytical approach that obtains force constants through perturbation theory analysis of equilibrium lattice geometries. Unlike the frozen phonon method, DFPT calculates crystal dynamical properties by computing the crystal's response to external energy perturbations, without requiring supercells or wavevector orthogonality to cell boundaries. DFPT provides a powerful computational tool for lattice dynamics analysis of complex crystals and is considered highly accurate, efficient, and reliable, though it requires specialized first-principles codes and modifications to the original programs—motivating our use of the open-source PHONONPY package. This work compares both methods for phonon DOS calculations in crystalline Al and Bi, whose structures are shown in [Figure 2: see original paper]. Al exhibits a typical FCC structure, while Bi belongs to the rhombohedral system.

In the NJOY thermal scattering law generation process, several operational details require attention. [Figure 3: see original paper] shows the specific steps for generating ACE-format thermal neutron scattering law databases using NJOY. The MODER module converts original ENDF/B nuclide databases from decimal to binary format for computational efficiency. The RECONR module

then performs resonance reconstruction on the raw nuclide cross-section data with a reconstruction tolerance of 0.001, followed by Doppler broadening in the BROADR module with a thinning error of 0.001. The processed fast neutron data are then provided to the THERMR module, while the LEAPR module supplies processed ENDF/B-format thermal neutron scattering law data to THERMR. The THERMR module calculates thermal scattering matrices and other quantities, then sends the generated pointwise cross-section library in PENDF format to the ACER module to produce MCNP-compatible ACE-format libraries. ACER generates two files: a new MCNP neutron cross-section library file placed in the MCNP cross-section directory, and a path file added to the MCNP index file XSDIR for program access during calculations. The most critical modules in this workflow are LEAPR and THERMR; Doppler broadening has minimal impact, primarily providing basic scattering cross-section data, while thermal neutron scattering behavior within nuclides is determined by the scattering law data in the LEAPR module.

Currently, NJOY's thermal scattering law generation uses MAT numbers and reaction channel MT numbers referencing early ENDF/B-VI format definitions for moderator materials. However, the early ENDF/B-VI database had incomplete definitions for moderator materials, only covering commonly studied moderators, limiting NJOY's recognition (MAT numbers) for new moderator materials. This work redefines thermal scattering law MAT numbers and thermal cross-section MT numbers for Al and Bi following ENDF/B-VI format rules for use in NJOY's LEAPR and THERMR modules.

Beyond phonon DOS, NJOY requires input of basic parameters such as bound-atom cross sections. lists the bound-atom mass number A and various reaction cross-section values for Al and Bi. For these metallic crystals, coherent elastic scattering is significant. While Al's FCC structure has built-in coherent scattering calculations in NJOY, Bi requires reconstruction of crystallographic structure factors and modification of the THERMR module.

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3 Results and Discussion

3.1 Lattice Parameter Comparison This work employed VASP for geometric structure optimization of Al and Bi, using experimental values from the Pearson database as initial parameters for lattice parameters and atomic positions. Both generalized gradient approximation (GGA) and local density approximation (LDA) pseudopotentials were tested, with structural relaxation to the lowest energy state using VASP's optimization routines. The electronic energy convergence criterion was set to 1×10^{-5} eV with a plane-wave cutoff energy of 400 eV. The results are presented in , showing that GGA-optimized lattice parameters are closer to Pearson database experimental values than LDA results. Consequently, all subsequent phonon DOS calculations for Al and Bi in this work used structures optimized with GGA pseudopotentials.

3.2 Comparison of Phonon Dispersion Relations and Phonon Density of States Using the optimized Al and Bi lattice structures, this work calculated phonon DOS using the flexible open-source PHONONPY software combined with VASP. The exchange-correlation functional employed GGA-PBE with a final cutoff energy of 400 eV. Calculations used the periodic supercell method with a $4 \times 4 \times 4$ supercell, and Brillouin zone integration was performed on a $3 \times 3 \times 3$ Monkhorst-Pack k-point grid. Both FP and DFPT methods were used to compute phonon dispersion relations for Al and Bi. The results along different directions in the Brillouin zone are shown in [Figure 4: see original paper] and [Figure 5: see original paper], with lower branches representing acoustic modes and higher branches representing optical modes. For Al crystals, DFPT and FP results are essentially similar, both producing reasonable phonon DOS for thermal neutron scattering data generation. However, for Bi crystals, the FP method yields dispersion relations containing imaginary frequencies around the gamma point, likely due to insufficient supercell size or inadequate atomic relaxation in the primitive cell. Such results with imaginary frequencies must be avoided in calculations. The DFPT method produces Bi dispersion curves without imaginary frequencies, and thus the DFPT phonon calculations for Bi are used for thermal neutron scattering data investigation.

The calculated phonon DOS results for Al and Bi are compared with literature data in [Figure 6: see original paper] and [Figure 7: see original paper]. Since phonon DOS units differ between ENDF/B-VIII.0, FP, and DFPT results, this work selects normalized phonon DOS on a β-grid for comparison. For Al, phonon DOS from FP, DFPT, and ENDF/B-VIII.0 show consistent overall trends, with DFPT showing better agreement with ENDF/B-VIII.0 in the low-energy region on logarithmic plots. For Bi, acoustic and optical branches are clearly separated, with calculated DOS values of zero in the 0.008–0.009 eV range, attributed to Bi's structure differing from simple cubic lattices. The DFPT results for Bi show better agreement with experimental phonon DOS from W. Kress for acoustic modes compared to Hawari's calculations, while optical modes are consistent with Hawari's results but with lower peak values and smaller broadening. Both calculations show slight deviations from experimental values, possibly due to insufficient atomic relaxation in primitive cells and experimental measurement errors. Overall, the DFPT method for phonon DOS generation is more flexible and reliable.

3.3 Thermal Neutron Scattering Cross-Section Data Comparison Based on phonon DOS from both FP and DFPT methods, this work completed thermal neutron scattering cross-section calculations for Al crystals using NJOY. The comparison of cross sections from different phonon DOS models is shown in [Figure 8: see original paper]. The incoherent inelastic scattering cross section from FP phonon DOS is higher than the DFPT result, with DFPT showing closer agreement with ENDF/B-VIII.0, particularly in the 10^{-9} to 10^{-7} MeV range. For both incoherent inelastic and coherent elastic scattering cross sections, DFPT shows better agreement with ENDF/B-VIII.0 than FP,

with differences between FP and DFPT increasing at higher energies, while DFPT remains consistent with ENDF/B-VIII.0. This indicates that DFPT phonon DOS better matches the phonon DOS employed in ENDF/B-VIII.0 for thermal neutron scattering characteristics.

Conclusion

Using Al and Bi metals as examples for thermal neutron cross-section generation, this work employed both frozen phonon (FP) and density functional perturbation theory (DFPT) methods with VASP combined with PHONONPY to calculate phonon dispersion relations and phonon DOS. Using the NJOY program with added Bi coherent scattering treatment in LEAPR, thermal neutron scattering cross-section libraries for Al and Bi were successfully generated. The results demonstrate that for Al, DFPT-derived phonon DOS produces thermal neutron scattering cross sections in better agreement with ENDF/B-VIII.0 compared to the FP method. For Bi, the DFPT method eliminates imaginary frequencies observed in FP calculations and yields thermal neutron scattering results that agree well with experimental values. This study proposes a more fundamental and predictive approach for generating thermal neutron cross sections from the perspective of exploring intrinsic material mechanisms, establishing a theoretical foundation for investigating thermalization mechanisms of nuclear materials in advanced reactor designs.

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Note: Figure translations are in progress. See original paper for figures.