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Analytical study on the size effect of phonon spectral energy density resolution

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ABSTRACT

Phonon spectral energy density (SED) is widely used in phonon mode analysis, from which the phonon dispersion curve and phonon lifetime of each vibration mode can be obtained. In practice, SED can be calculated through time–space 2D Fourier transforms of the velocity fields of atoms from molecular dynamics (MD) simulations (Maruyama, 2003) [1]. However, the resolution of phonon SED is not satisfactory for limited-size systems. Although previous works have highlighted this problem, a quantitative relationship is still lacking for how the resolution of phonon SED changes with the size of the simulation domain. In this work, we analytically derived the relationship using the convolution theorem in Fourier transforms. Moreover, molecular dynamics simulations were performed in a 1D atom chain to prove our derivation. Then, we drew a conclusion to guide the simulation settings in the MD simulations to achieve a reasonable resolution at the end of this article.

1. Introduction

Phonon behavior is of fundamental importance in studies of material properties because of its coupling with other quasi-particles. To analyze the behavior of phonons, the phonon spectrum plays an important role. It provides us with the energy of different phonon modes in momentum space. Several different methods have been proposed to calculate the phonon spectrum. For example, a force constants matrix can be successfully obtained using density functional perturbation theory [2] (DFPT) and the dielectric method [3]. Another method called the frozen phonon method [4] is also frequently used in phonon spectrum calculations, such as PHONOPY, and it is highly compatible with existing first principles calculation packages.

However, most of the aforementioned methods are static, zero-temperature methods, and the anharmonicity is not completely included. In order to obtain the phonon property at different temperatures, the first-order perturbation theory [5] and renormalization theory [6] was used. Researcher also analyzed phonon property by combining Fourier transform and MD simulation [1,7]. Due to the anharmonic effect, both phonon frequency and phonon eigenvector can shift from their harmonic values [8]. Over the past several years, phonon spectral energy density (SED), which was used in the study mentioned before [8], has become a powerful tool in studies of phonon behavior. Because phonon SED is based on a 2D Fourier transformation of the atomic velocity fields, it contains the vast majority of information about the dynamics for different temperatures, including the effect of anharmonic terms. With phonon SED, we can calculate the frequency and the phonon lifetime of each vibration mode of systems with complex structures at finite temperature. Phonon SED has been successfully used in the phonon mode analysis of many nanostructures, e.g., one-dimensional graphyne nanotubes [9], two-dimensional silicene [10], one-dimensional graphene [11], and so forth. Moreover, phonon SED can also be performed even in disordered systems [12] without the phonon mode eigenvectors. In these simulations, the authors studied different sized domains; one of the reasons is to is to achieve sufficient resolution of SED in momentum space [13]. Although this point was well recognized by previous researchers,they only investigated sufficiently large samples to avoid smearing of the spectrum in their studies. Furthermore, the criterion for the 'sufficient size' was not mentioned.

Therefore, in our work, we analytically established the relationship between the size of the simulation domain and the resolution of the SED. This derivation was performed with the help of convolution theory. Moreover, molecular dynamics studies of series of single atom chains with different lengths were conducted, and

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the following SEDs were obtained from the velocity fields of such atoms. In this simple case, the corresponding broadening of the spectrum was extracted, and they fit quite well with our analytical formula. Finally, we attempted to provide the expression for the 'sufficient size' criterion.

In the calculation of the phonon SED function Φ, the following formula is used [14]

$$\Phi(\boldsymbol{k},\omega)=\frac{1}{4\pi\tau_0}\sum_{\alpha}^{3}\sum_{b}^{n}\frac{m_b}{N}\left|\sum_{l}^{N}\int_0^{\tau_0}\dot{u}_\alpha(l,b,t)exp[\Theta]dt\right|^2 \quad (1)$$

where $\boldsymbol{k}$ is the wave vector in momentum space, ω is the frequency, τ_0 is the total integration time, and α denotes the x, y, and z directions. There are N unit cells in the system, with n atoms each. m_b is the mass of the bth atom in the unit cell. $\dot{u}_\alpha(l,b,t)$ is the α component of the velocity of the bth atom in the lth unit cell. Θ is defined as $i[\boldsymbol{k}\cdot\boldsymbol{r}_0(l)-\omega t]$, where $\boldsymbol{r}_0(l)$ is the equilibrium position vector of the lth unit cell. Apparently, the calculation of the phonon SED can be understood as a Fourier transformation of the velocity field of all the atoms in the sample, and thus, the phonon SED reflects the strength of vibrations in a material.

In Fig. 1, we present the phonon spectral energy densities for one-dimensional chains that are 10-nm long ($N_z=20$) and 50-nm long ($N_z=100$). The atomic velocities were obtained from NVE MD simulations with periodic boundary conditions at a temperature of 1 K using LAMMPS. The interactions between atoms (mass equal to 14.02 g/mol) are simply set as harmonic bondings with bond coefficients of 5.9 and 5.0 in real units in LAMMPS. The time step of the MD simulations is 1 fs, and we extracted velocities every 20 time steps. The sampling rate of $0.05fs^{-1}$ was determined according to the sampling theorem, which shows that the sampling rate should be two times greater than the highest phonon frequency to avoid aliasing. Prior to sampling, the system needs to be fully relaxed and achieve equilibrium. The phonon SED can be fit with a Lorentzian function in the frequency domain [14], as in Eq. (2). If one want to calculate the phonon life time, the total integration time in the phonon SED calculation should be more than five times greater than the longest phonon lifetime τ_{max}, which can be determined from the above fitting; see Eq. (3):

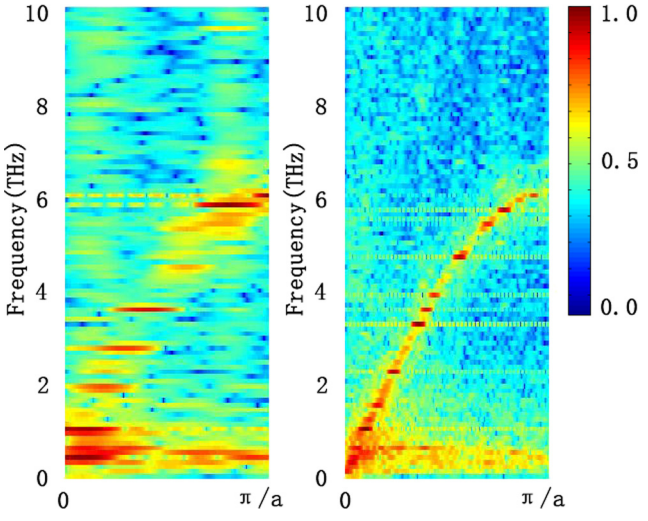

Fig. 1. The picture on the left is the phonon SED of a 10-nm-long ($N_z=20$) one-dimensional chain at a temperature of 1 K. The picture on the right is the phonon SED of a 50-nm-long ($N_z=100$) one-dimensional chain at a temperature of 1 K. The shading indicates the magnitude of phonon SED for wave vector $\boldsymbol{k}$ and frequency ω. It is obvious that the resolution of phonon SED changes with the size of the system. Although a hamming window was used to reduce spectrum leakage, these leakage are still visible for low frequency.

$$\Phi(\boldsymbol{k},\omega)=\frac{I}{1+\left(\frac{\omega-\omega_0}{\gamma}\right)^2} \quad (2)$$

$$\tau_{max}=\frac{1}{2\gamma} \quad (3)$$

where $\boldsymbol{k}$ is the wave vector, I is the peak magnitude, ω_0 is the frequency at the peak center, and γ is half-width at half-maximum. Fig. 1 clearly shows that the resolution of the phonon SED of the 100 atom chain is higher than that of the 20 atom chain. In our simulation, our total sampling time is set as 1 ns which is much smaller than the longest phonon lifetime (theoretically, infinitely large) because there is no need for phonon lifetime in our research. To understand how the size of the simulation domain affects the resolution of phonon SED, a schematic diagram is presented in Fig. 2.

To calculate the velocity field from an infinite sample, the simulation domain should be infinitely long in principle. This is impossible in real calculations, and it can be avoided by introducing periodic boundary conditions (PBCs). With the help of PBCs, the information of an infinite sample can be obtained from a limited-size sample. At the same time, the information that we obtained from the simulation domain, the velocity field for example, can be understood as the information from the original infinite sample times a rectangular function with the same length as the simulation domain, shown in Fig. 2(a) and (b). In other words, we multiply the velocity field function by a rectangular window function in a space domain of width L, with a value of 1 inside the box and 0 outside of the box, as shown in Fig. 2(b).

The rectangular window function can be expressed as follows:

$$w(x)=\begin{cases}1 & : \quad x\in[0,L]\\ 0 & : \quad else\end{cases}$$

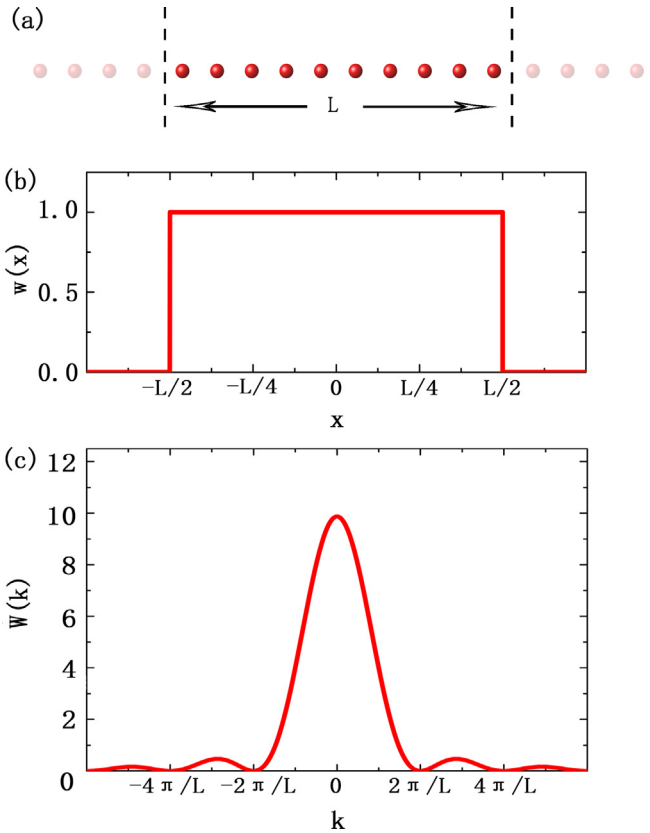

Fig. 2. (a) The simulation box under periodic boundary conditions. The length of the box is L. (b) A rectangular window function in real space. (c) The Fourier transform of the rectangular window function.