

Relaxation of Phonons in Classical MD Simulation*

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Abstract

We propose a novel technique of molecular dynamics simulation to evaluate the relaxation time of phonons in solids for investigation of solid heat conductivity. The basic idea is to observe relaxation behavior of the power spectrum of atomic velocities after energetically stimulating modes in a specific frequency region. The transient entropy $S(t)$ is defined with the power spectrum based on non-equilibrium statistical mechanics to quantitatively evaluate the relaxation speed. In this paper, two example systems are shown; Lennard-Jones model crystal and silicon crystal. For both systems, we found that the observed $S(t)$ is well fitted to a single exponential function, from which we can obtain a frequency-dependent relaxation time.

Key words : Phonon relaxation, Molecular Dynamics Simulation,
Non-Equilibrium Entropy, Thermal Conductivity in Solids

1. Introduction

As the typical size of semiconductor devices becomes smaller, heat transfer analyses and thermal designs are becoming harder.⁽¹⁾ In extreme cases, such as high-k insulator thin films and SOI (silicon on insulator) with strained silicon, the characteristic size is much less than the mean free path of phonons, and the heat transfer should be analyzed on ballistic phonon basis, not on diffusive heat conduction basis.

To analyze the phonon transport phenomena, the Boltzmann transport equation for the phonon distribution function f is often utilized.^{(1),(2)} Under an external field \vec{F} , the equation is in general expressed as

$$\frac{\partial f(\vec{r}, \vec{p}, t)}{\partial t} + \vec{V} \frac{\partial f}{\partial \vec{r}} + \vec{F}(\vec{r}) \frac{\partial f}{\partial \vec{p}} = \left(\frac{\partial f}{\partial t} \right)_{coll} \quad (1)$$

where the time-dependent f is a function of the position \vec{r} and momentum \vec{p} of phonons. The term on the right hand side represents the “scattering” due to phonon-phonon or phonon-electron interactions, which causes the relaxation to the equilibrium distribution f_{eq} . This relaxation is in principle a very complicated process, and the following linearized approximation, or “relaxation time approximation”, is often assumed^{(1),(2)}

$$\frac{\partial f}{\partial t} + \vec{V} \frac{\partial f}{\partial \vec{r}} \simeq - \frac{f - f_{eq}}{\tau} \quad (2)$$

Here we also omit the external force term, assuming that the system is uniform with no external field. This linearized Boltzmann equation is very simple and convenient for numerical analyses of heat transfer in various solid systems.

The relevant parameter here is the relaxation time τ , which should in principle depend on the frequency and the mode (e.g., longitudinal, transverse, acoustic, optical, etc.) of each phonon. In solid-state physics, many researches have been done on the phonon relaxation processes,⁽²⁾⁻⁽⁴⁾ but it is not an easy task to evaluate τ for a given system.

In this paper, we propose a new approach to estimate τ as a function of the phonon frequency using molecular dynamics (MD) simulation technique. Our strategy is to make a non-equilibrium state and to observe the relaxation of f directly with classical MD simulation. Comparing with Eq. (2), we will be able to evaluate τ .

2. Nomenclature

c : magnification factor of energy excitation [-]	\vec{V} : phonon velocity [m s^{-1}]
\vec{F} : external force [N]	ϵ : Lennard-Jones energy parameter [J]
f : phonon distribution function [-]	ϕ : particle-particle interaction potential [J]
\vec{p} : momentum coordinate [kg m s^{-1}]	σ : Lennard-Jones size parameter [m]
\vec{r} : spatial coordinate [m]	τ : phonon relaxation time [s]
S : entropy [J K^{-1}] or [-]	ω : angular frequency [s^{-1}]
t : time [s]	

3. Method

The basic procedure here proposed for estimating τ of a given system consists of the following six steps:

- (1) The equilibrium state of our target is first generated with a normal MD simulation.
- (2) Lattice vibration analysis is done with a Fourier transform technique using the atomic velocity data.
- (3) Atomic vibrations with a given range of frequency are artificially excited, i.e., the Fourier coefficients of the given range are magnified by some factor.
- (4) An excited state is generated with an inverse Fourier transform of the above-modified vibrations.
- (5) Non-equilibrium MD simulation is executed with the excited state as the initial condition.
- (6) Relaxation of the power spectrum is investigated by using a Fourier transform with a small time window.

The idea seems simple, but several issues are raised, such as how large the “magnification factor” at Step (3) should be for the excitation. To demonstrate how the procedure works, we here report two simple systems, i.e., argon FCC crystal at extremely low temperature and silicon crystal (diamond structure) at room temperature.

4. Argon Crystal

4.1. Simulation system

The first example is FCC single crystal of argon-like monatomic molecules interacting via the Lennard-Jones (12-6) potential:

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3)$$

where r is the distance between particles. We have chosen $\epsilon = 1.67 \times 10^{-21}$ J and $\sigma = 0.34$ nm as the potential parameters.

The crystal is a cube of $5.44 \text{ nm} \times 5.44 \text{ nm} \times 5.44 \text{ nm}$, composed of 4,000 particles. The periodic boundary conditions are assumed for all directions, and the interactions are truncated at $r = 1.2 \text{ nm}$.

The MD simulation was done at 1.4 K, which is much lower than the melting point (about 80 K under the normal pressure). We chose this extremely “cold” state so that we can trace a sufficiently slow relaxation process with our proposed scheme.

4.2. Density of states

After equilibrating the system, atomic velocity data were accumulated for 40 ps (10000

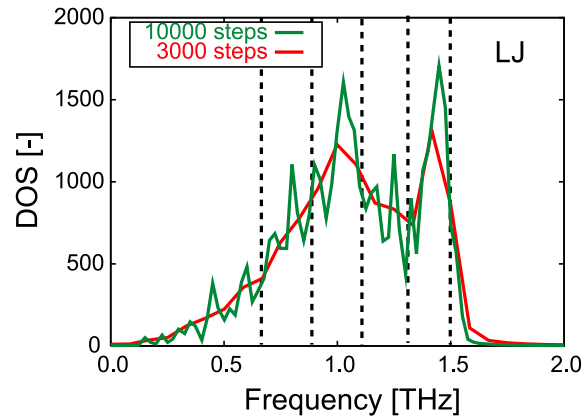


Fig. 1 DOS of argon crystal at equilibrium.

steps). The power spectrum, or the density of vibrational states (DOS) is calculated as

$$f_{eq}(\omega) = \left\langle \left| \frac{1}{t} \int_0^t \vec{v}(t') \exp[i\omega t'] dt' \right|^2 \right\rangle \quad (4)$$

where $\langle \dots \rangle$ means the average over all particles. The result is shown in Fig. 1. The result of Fourier transform with shorter period (12 ps, or 3000 steps) is also shown because this short period will be adopted in the transient Fourier analysis at the later steps.

The DOS has two apparent peaks, a broad one at $\omega/2\pi \approx 1.0$ THz and a rather narrow one at 1.4 THz, which roughly correspond to transversal and longitudinal modes, respectively.

4.3. Mode excitation

Referring to $f_{eq}(\omega)$, we chose four ranges of frequency to be excited:

- Region 1: $0.7 \text{ THz} \leq \omega/2\pi \leq 0.9 \text{ THz}$
- Region 2: $0.9 \text{ THz} \leq \omega/2\pi \leq 1.1 \text{ THz}$, corresponding to the first peak
- Region 3: $1.1 \text{ THz} \leq \omega/2\pi \leq 1.3 \text{ THz}$
- Region 4: $1.3 \text{ THz} \leq \omega/2\pi \leq 1.5 \text{ THz}$, corresponding to the second peak

We energetically excite the modes in each region by a constant factor c ; in other words, the Fourier coefficient of each atomic velocity is multiplied by a constant \sqrt{c} . The choice of c is the crucial part of our scheme. One hand, c should be close to unity so that the artificial excitation does not change the system state very much from the equilibrium. On the other hand, we have to prepare such a non-equilibrium state that we can trace the relaxation with sufficiently large S/N ratio. We tried three cases, $c = 0, 2$, and 10 , among which $c = 10$ was found to be the most suitable for our purpose.

4.4. Relaxation

With the excited state as the initial conditions, we carry out a microcanonical MD simulation. The system relaxes to the equilibrium state during the simulation, and we trace the process by monitoring the change of power spectrum, which is obtained by a short-time Fourier transform of atomic velocity data with period of 12 ps.

4.5. Power spectrum change

Examples of the relaxation process are shown in Fig. 2, where results of Region 2 and Region 4 are depicted. Since the MD calculation is done with the microcanonical (i.e., energy-constant) condition, the energy input in the excited frequency region is transferred to other modes. As was expected, the speed of relaxation seems to depend on the frequency; relaxation in Region 4 seems much faster than in Region 2.

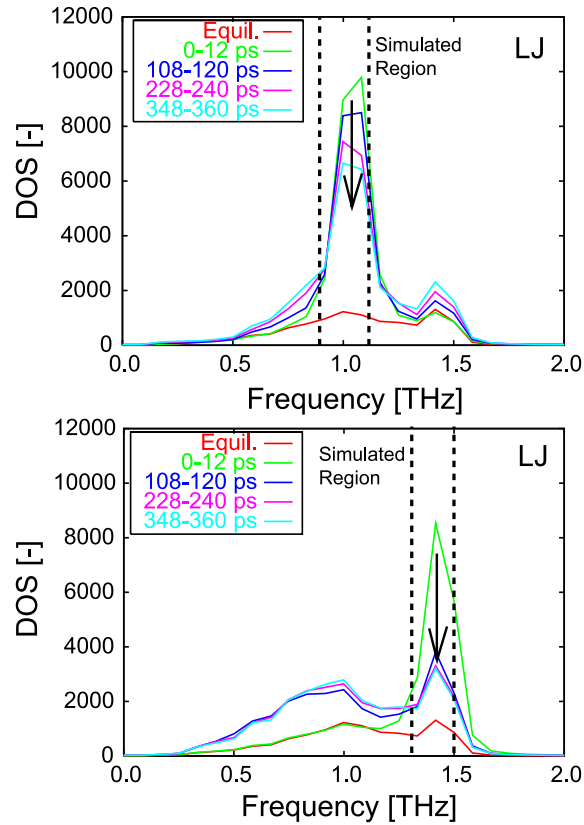


Fig. 2 Examples of DOS relaxation after excitation of specific modes; argon crystal. The excited region is (top) $0.9 \text{ THz} \leq \omega/2\pi \leq 1.1 \text{ THz}$, (bottom) $1.3 \text{ THz} \leq \omega/2\pi \leq 1.5 \text{ THz}$.

4.6. Non-equilibrium entropy

To evaluate the relaxation time quantitatively, we define “non-equilibrium entropy” as⁽⁵⁾

$$S(t) = - \int f(\omega; t) \log \left[\frac{f(\omega; t)}{f_{eq}(\omega)} \right] d\omega \quad (5)$$

Here we treat $S(t)$ as a dimensionless quantity by omitting the Boltzmann constant k_B because we focus only on its relative relaxation.

The results are shown in Fig. 3; the relaxation speed is different for different frequency region. We found that the data are well fitted to a single exponential function,

$$S(t) \sim S_0 \exp[-t/\tau] \quad (6)$$

with S_0 and τ as fitting parameters, from which we obtain the relaxation time τ . The results are shown in Fig. 4.

The obtained relaxation time for the argon crystal at 1.4 K is a strongly decreasing function of the frequency; its typical value is ~ 200 ps at 1.0 THz (the period is 1 ps) and ~ 20 ps at 1.4 THz (0.71 ps). Considering that the DOS has a maximum around 1 THz and that the group velocity of phonons is almost constant for the region of $\omega/2\pi \leq 1.5 \text{ THz}$ ⁽⁶⁾, we estimate that the averaged τ of phonons relevant to the thermal conductivity is 100–200 ps.

The value is much larger than what we reported in Ref. (6) with a wavelet analysis technique ($\tau \approx 1 - 20$ ps for argon crystal at $T \approx 24$ K). This is partly because the temperature in this work (1.4 K) is so low that the anharmonicity of atomic interactions causing the phonon relaxation is very weak.

5. Silicon Crystal

The second demonstration is silicon single crystal with the diamond structure. Rough estimation using the data of thermal conductivity, specific heat, and sound speed at the room

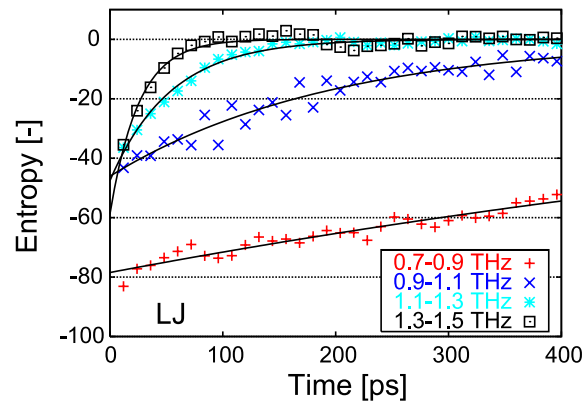


Fig. 3 Entropy change during the relaxation; argon crystal. Curves are the least square fit to a single exponential function.

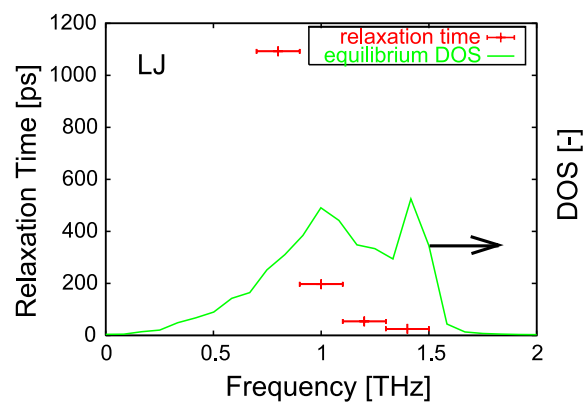


Fig. 4 Frequency-dependent relaxation time of argon crystal.

temperature⁽⁷⁾ gives $\tau \sim 2\text{--}5$ ps. Similarly to the argon case, however, we expect some frequency dependence. Narumanchi et al.⁽⁸⁾ recently proposed a detailed phonon-dispersion model with strongly frequency-dependent relaxation time. As a preliminary demonstration of our method, we applied it to silicon crystal at room temperature.

5.1. Simulation system

Tersoff potential⁽⁹⁾ was adopted for the simulation. We used a fairly large cubic crystal of $10.8\text{ nm} \times 10.8\text{ nm} \times 10.8\text{ nm}$, which consists of 64,000 silicon atoms. After equilibrating the system at $T = 300\text{ K}$, we obtained the DOS with a procedure similar to the argon case, as shown in Fig. 5. Since the lattice structure is more complicated than argon, there are several

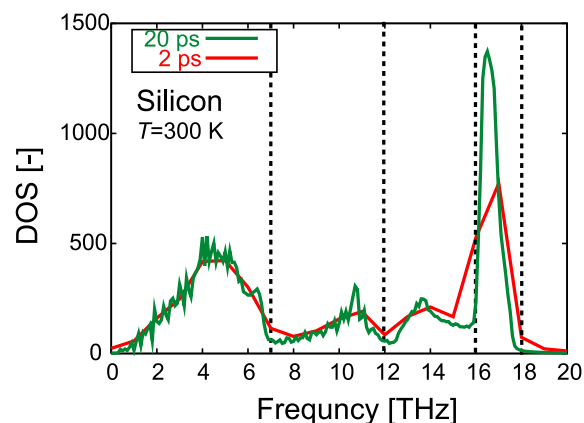


Fig. 5 DOS of silicon crystal at equilibrium.

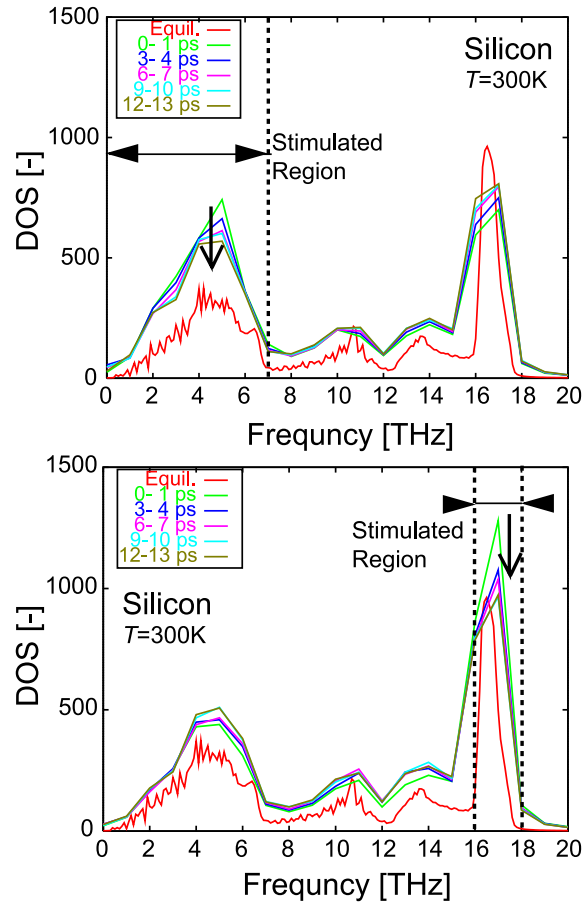


Fig. 6 Examples of DOS relaxation after excitation of specific modes; silicon crystal. The excited region is (top) $0 \text{ THz} \leq \omega/2\pi \leq 7.0 \text{ THz}$, (bottom) $16.0 \text{ THz} \leq \omega/2\pi \leq 18.0 \text{ THz}$.

peaks corresponding to acoustic and optical phonon modes.

5.2. Mode excitation

Four regions were separately investigated, corresponding to each of four peaks:

- Region 1: $0 \text{ THz} \leq \omega/2\pi \leq 7 \text{ THz}$
- Region 2: $7 \text{ THz} \leq \omega/2\pi \leq 12 \text{ THz}$
- Region 3: $12 \text{ THz} \leq \omega/2\pi \leq 16 \text{ THz}$
- Region 4: $16 \text{ THz} \leq \omega/2\pi \leq 18 \text{ THz}$

We tried the magnification factor as $c = 3$, smaller than the argon case.

5.3. Relaxation

With a similar procedure to argon, we observed the DOS spectrum change. Examples are shown in Fig. 6, where excitation in Region 1 and excitation in Region 4 are depicted. It is interesting that the Region 1 and Region 4 seem to have a strong coupling; as the enhanced energy in Region 1 relaxes, the energy in Region 4 increases with a similar rate, while the energy in Regions 2 and 3 varies little.

5.4. Entropy change

Figure 7 shows the non-equilibrium entropy defined in Eq. (5). Although it contains large fluctuations probably due to our choice of the small magnification factor ($c = 3$), we see clear dependence of the relaxation speed on the frequency. Typical values are $\tau = 1\text{--}2 \text{ ps}$ for the high frequency ($7 \text{ THz} \leq \omega/2\pi$) modes, roughly corresponding to the empirical values. To improve the S/N ratio, larger c and more statistical average will be required.

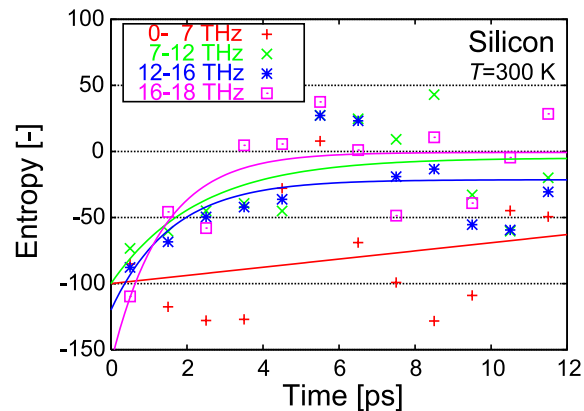


Fig. 7 Entropy change during the relaxation; silicon crystal.

6. Discussion

One of the key points in our scheme is the definition of the transient entropy $S(t)$ to quantitatively evaluate τ . As in the Boltzmann's H theorem,⁽⁵⁾ it is easily proved that $S(t)$ decays as a single exponential function of t when the distribution f strictly obeys the linearized equation, Eq. (2). However, in our scheme, the relaxing dynamics of f is turned out to be rather complicated due to the interaction among phonons with different frequencies (and modes), as pointed out in Sec. 5.3. We found that it is still useful to use $S(t)$ even for the case of complicated phonon-phonon interactions.

Concerning investigation of phonons with MD simulation, there are several other approaches. Schelling et al.⁽¹⁰⁾ proposed a direct observation of wave packet propagation to evaluate transmission and scattering of phonons at a semiconductor interface. Since they adopt spatially-localized and mode-specific wave packets, it is more suitable to interfacial phenomena⁽¹¹⁾ than relaxation in “bulk” solid. The autocorrelation function method is an alternative, which has been adopted by McGaughey et al.⁽¹²⁾ for energy relaxation. They combined it with the normal mode analysis, which enabled them to investigate a more detail of mode-mode coupling behavior⁽¹³⁾. Their scheme has a merit that good ensemble average is obtained more easily since the autocorrelation is evaluated under an equilibrium state. We also tried a similar autocorrelation function method for atomic displacements with wavelet analysis,⁽⁶⁾ and with normal mode analysis,⁽¹⁴⁾ to some limited success. Compared with these schemes, the method proposed in this paper seems more straightforward, less laborious, and more robust to noises, although it may be a little bit harder to be more mode-specific.

Our method has so far revealed a strong frequency dependence of the phonon relaxation time $\tau(\omega)$. Naïvely speaking, some sort of average over ω would give a more reliable relaxation time τ , which can be used in evaluation of thermal conductivity appearing in the Fourier's law of heat conduction. As described in Sec. 1, however, our main target is the systems which we should take account of ballistic phonon transports. For that purpose, there emerge two possible ways of using the finding. When we replace τ in Eq. (2) with the frequency-dependent τ , we expect to have more precise evaluation of phonon transport and heat transfer processes; this is more practical as thermal engineering. The second one, which is rather fundamental as thermal science, is to re-examine the linear approximation, i.e., derivation of Eq. (2) from Eq. (1), by more closely looking into the correlation among various modes, as mentioned in Sec. 5.3.

7. Conclusion

To evaluate the phonon relaxation time for the Boltzmann transport equation in crystalline solids, we developed a new scheme of directly observing a process of power spectrum relaxation from a specific excited state with non-equilibrium molecular dynamics simulation and a lattice vibration analysis. Two examples, i.e., argon FCC crystal and silicon crystal, were

shown as a demonstration, and strong dependence on the phonon frequency was observed in both systems.

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