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Physics of Phonons in Amorphous C-S-Hs

THESIS

submitted in partial satisfaction of the requirements
for the degree of

MASTER OF SCIENCE

in Mechanical and Aerospace Engineering

by

Yun Zhou

Thesis Committee:
Assistant Professor Jeaho Lee, Chair
Assistant Professor Mohammad Javad Abdolhosseini Qomi
Assistant Professor Yoonjin Won

2016

DEDICATION

To

My parents, and friends and mentors,

who have been vital to my success

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ACKNOWLEDGMENTS

I would like to express my deep appreciation to faculty advisor, Professor Lee, who has the attitude and the substance of a genius: he continually and convincingly conveyed a spirit of adventure in regard to research and scholarship, and an excitement in regard to teaching.

In addition, I would also like to express my gratitude to Prof. Abdolhosseini, without whose guidance and persistent help this thesis would not have been possible.

Lastly, I would like to thank my parents who have always supported and inspired me.

ABSTRACT OF THE THESIS

Physics of Phonons in Amorphous C-S-Hs

By

Yun Zhou

Master of Science in Mechanical Engineering

University of California, Irvine, 2016

Professor Jaeho Lee, Chair

In this master thesis, we have probed the heat transport in C-S-Hs by both molecular dynamics simulations and phonon eigenvalue analyses. Green-Kubo method is used in molecular dynamics simulations to compute the heat flux and thermal conductivity in C-S-Hs. Noting that C-S-H is relatively amorphous, both propagating modes and nonpropagating modes of phonons are considered in analytical analyses. Bose-Einstein transport equation is used to compute the contribution to the total thermal conductivity from each propagating eigenmode of phonon vibration, while AF theory is applied to investigate the nonpropagating modes of C-S-H. GULP analyses have been performed on C-S-H samples, giving us the eigenfrequencies and eigenvectors of phonons in the system. The participation ratios, group velocities, relaxation times and mode diffusivities of phonons are studied. After comparing our simulation results with analytical analyses, we found that the heat transport phenomenon in amorphous C-S-Hs can be well explained by the combination of BTE equation and AF theory.

INTRODUCTION

Cement is one of most important and commonly used manmade construction materials on earth. While research has been done on cement's mechanical properties [1-3], its thermal properties at the nanoscale are still obscure, which attract our attention. Cement's thermophysical properties are recognized to be important for both construction and use phases [4]. During cement's exothermic hydration process, thermal stresses may cause early-age cracking, which may compromise the long-term serviceability of structures. The dimensional arguments indicate that these thermal stresses are inversely proportional to the thermal diffusivity of cement paste. During the use phase, the thermophysical characteristics of concrete (and all other construction materials) affect the heating and cooling energy consumption of buildings via either heat conduction through the envelope or the thermal mass of the buildings, i.e., the tendency of a building to maintain a constant temperature despite outdoor temperature oscillations. Both aggregates and the cement paste affect the thermal properties of concrete, however, the former is the dominant factor. Despite the importance of thermal properties of concrete, such studies are truly scarce and are limited to the macroscopic measurement of thermal properties of concrete and cement paste. More specifically, the interplay between chemistry and molecular properties of cement paste's constituents and their relation to macroscopic properties remain rather obscure.

Previous study [4] has shown that amorphous C-S-H has relatively low thermal conductivity compared with some other materials such as silicon. In order to investigate the physics behind its heat transport, we performed molecular dynamics simulations along with phonon eigenvalue analyses in our study. Green-Kubo method is used in molecular dynamics simulations to compute the thermal conductivity. To investigate the contribution to the total thermal conductivity that comes from each phonon vibration modes, we did phonon eigenvalue analyses using the software GULP. The participation

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ratios, group velocities and relaxation time are obtained using the results from MD simulations and phonon eigenvalue analyses. Boltzmann transport equation [5] is used to investigate the part of thermal conductivity that comes from propagating phonon vibration modes. Because our system is amorphous and disordered, AF theory [6-7] is applied to obtain the mode diffusivity and thermal conductivity that are from nonpropagating vibration modes. By comparison of the results from molecular dynamics and the analytical model, we drew the conclusion that the heat transport in C-S-Hs can be well described by the phonon vibrations of propagating and nonpropagating modes.

The rest of this thesis is organized as follows: in section 2, the basic concepts of phonon and molecular dynamics simulation are introduced; in section 3, our research topic, research model, and hypothesis are proposed; in section 4, we perform a series of MD simulations on 7 independent C-S-H samples, and analytical analyses of thermal conductivity of C-S-Hs will be carried out; in section 5, we complete this master's thesis with results and discussion.

THEORY BACKGROUND

Lattice Vibrations: Phonons

A phonon is a quantum mechanical description of an elementary vibrational motion in which a lattice of atoms or molecules uniformly oscillates at a single frequency [8]. It is a collective excitation in a periodic, elastic arrangement of atoms or molecules in solids or some liquids. In classical mechanics this designates a normal mode. Normal modes are important because any arbitrary lattice vibration can be considered to be a superposition of these elementary vibrations. The concept of phonons was introduced in 1932 by Soviet physicist Igor Tamm. The name phonon comes from the Greek word φωνή (phonē), which translates to sound or voice because long-wavelength phonons give rise to sound. Shorter-wavelength higher-frequency phonons give rise to heat. Phonons play a significant role in many of the physical properties of a material, such as thermal conductivity and electrical conductivity.

For a classical, vibrating system the harmonic approximation corresponds to considering only vibrations with small amplitude. For such small amplitudes, the potential, in which the particle (or the particles) is/are moving, can be expanded in a Taylor series around the equilibrium geometry, keeping only the first leading term. To illustrate this, consider the classic example of the one-dimensional harmonic oscillator. The general Taylor expansion around a minimum at

$$V(x) = V(x_0) + \left[\frac{\partial}{\partial x}V(x)\right]_{x_0} s + \frac{1}{2}\left[\frac{\partial^2}{\partial x^2}V(x)\right]_{x_0} s^2 + \frac{1}{3!}\left[\frac{\partial^3}{\partial x^3}V(x)\right]_{x_0} s^3 + \cdots \ , (1)$$

with the displacement $s = x - x_0$. The linear term vanishes, because x_0 is an equilibrium geometry. For small displacements, the cubic (and higher) terms will be comparably small, leaving in the harmonic approximation only

$$V(x) \approx V(x_0) + \frac{1}{2}\left[\frac{\partial^2}{\partial x^2}V(x)\right]_{x_0} s^2 \ . \tag{2}$$

Therefore, we get the following expression for the restoring force for a given displacement s

$$F = -\frac{\partial}{\partial x}V(x) = -cs \ , \tag{3}$$

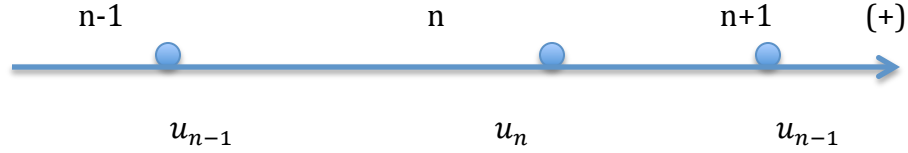where $c = \left[\frac{\partial^2}{\partial x^2} V(x)\right]_{x_0}$.

Figure 1 Vibrations of a linear one-atomic chain (displacements).

Consider an infinite one-dimensional linear chain of atoms of identical mass m, connected by springs with (constant) spring constant c, as shown in Fig.1. The distance between two atoms in their equilibrium position is a, and u_n the displacement of then nth atom from this equilibrium position. According to the quasi-elastic approximation Eq. (3), the Newton equation of motion for this system is written as

$$m\ddot{u}_n + c(2u_n - u_{n-1} - u_{n+1}) = 0. \tag{4}$$

Noting that the Eq. (4) does not change if we shift the system as a whole by a times an integer, the solution to this equation becomes

$$u_n = Ae^{i(qan-\omega t)}. \tag{5}$$

It's a plane wave for discrete coordinates na. By substituting Eq. into Eq, we can immediately get

$$\omega = \omega_m \left|\sin\frac{qa}{2}\right|, \omega_m = 2\sqrt{\frac{c}{m}}. \tag{6}$$

The expression above is called the dispersion law. It differs from the dispersion relation for an homogeneous string, $\omega = sq$. If we replace the wave number q as $q' = q + \frac{2\pi g}{a}$, where g is an integer, the solution does not change. Therefore, if we choose the region

$$-\frac{\pi}{a} \le q \le \frac{\pi}{a}, \tag{7}$$

we can represent the dispersion law in the whole q-space.

At small q we get $\omega = sq$, where $s = a\sqrt{\frac{c}{m}}$, is the sound velocity in a homogeneous elastic medium. In a general case, the sound velocity becomes q-dependent because

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of the dispersion of the waves. Phase velocity V_p and group velocity V_g are defined as

$$V_p = \frac{\omega}{|q|} = s\left|\frac{\sin\left(\frac{aq}{2}\right)}{\frac{aq}{2}}\right|,\tag{8}$$

$$V_g = \frac{d\omega}{dq} = s|cos(aq/2)|.\tag{9}$$

For the vibrations of a compound lattice, using the same method, we can get the displacement equations for the two atoms as

$$u_n = A_u e^{i(qan-\omega t)}, v_n = A_v e^{i(qan-\omega t)}.\tag{10}$$

To express these equations in a matrix form, we introduce the vector $\boldsymbol{A} = (A_u\ A_v)$ and the dynamic matrix of the vibration system

$$\widehat{D} = \begin{pmatrix} \frac{c_1+c_2}{m_1} & -\frac{c_1+c_2 e^{-iaq}}{m_1} \\ -\frac{c_1+c_2 e^{-iaq}}{m_2} & \frac{c_1+c_2}{m_1} \end{pmatrix},\tag{11}$$

where m_1 and m_2 are the masses of the 2 atoms, respectively.

The equation for A has the form

$$\omega^2 \boldsymbol{A} - \widehat{D}\boldsymbol{A} = 0 \,.\tag{12}$$

From the equation above, we get ω^2 and corresponding eigenvectors, which are the eigenvalues (eigenfrequencies) and eigenvectors of dynamic matrix $\widehat{D}$.

3D lattice vibration can be described by expansion of the 2D case. Similarly, we get the dynamic matrix

$$D_{\alpha\beta}^{kk'} = \sum_{n'} \frac{1}{\sqrt{m_k m_{k'}}} \Phi_{\alpha\beta}\begin{pmatrix} kk' \\ nn' \end{pmatrix} e^{iq(a_n'-a_n)}.\tag{13}$$

For a system with N atoms, the dynamic matrix has $3N$ eigenfrequencies and eigenvectors. Among these $3N$ eigenfrequencies, 3 are acoustic modes with $\omega = 0$, and $3N - 3$ are optical modes.

Molecular dynamics Simulation

Molecular dynamics [11,13] is a computer simulation for detailed microscopic modeling on the molecular scale. The method was originally developed within the

field of theoretical physics in the late 1950s [9,10], but is applied today mostly in chemical physics, materials science and the modeling of biomolecules.

Molecular dynamics simulation consists of the numerical, step-by-step, solution of the classical equations of motion, which for a simple atomic system may be written

$$m_i \ddot{r}_i = f_i \quad f_i = -\frac{\partial}{\partial r_i} \mathcal{U}. \tag{14}$$

In order to describe the motion of atoms we need to calculate the forces f_i acting on the atoms, which are usually derived from a potential energy $\mathcal{U}(\mathrm{r}^N)$, where $\mathrm{r}^N = (\mathrm{r}_1, \mathrm{r}_2, \dots \mathrm{r}_N)$ represents atom coordinates. The potential energy $\mathcal{U}$ consists of two parts, non-bonded potential $\mathcal{U}_{non-bonded}$ and bonding potential $\mathcal{U}_{intramolecular}$.

The part of the potential energy representing non-bonded interactions between atoms is traditionally split into 1-body, 2-body, 3-body... terms

$$\mathcal{U}_{non-bonded}(r^N) = \sum_i u(r_i) + \sum_i \sum_{j>i} v(r_i, r_j) + \cdots. \tag{15}$$

The $u(\boldsymbol{r})$ term represents an externally applied potential field or the effects of the container walls; it is usually dropped for fully periodic simulations of bulk system. Also, it is usual to concentrate on the pair potential and neglect three-body (and higher order) interactions. The Lennard-Jones [12] potential is one of the most commonly used forms

$$v^{LJ}(r) = 4\mathcal{E} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \tag{16}$$

where σ is the diameter, and $\mathcal{E}$ is the well depth.

In the simplest molecular model like shown in Fig.2, the intramolecular bonding interactions has the bonding potential as

$$\mathcal{U}_{intramolecular} = \frac{1}{2}\sum_{bonds} k_{ij}^r (r_{ij} - r_{eq})^2 + \frac{1}{2}\sum_{bend\ angles} k_{ijk}^\theta (\theta_{ijk} - \theta_{eq})^2 +$$
$$\frac{1}{2}\sum_{torsion} \sum_m k_{ijkl}^{\phi,m} (1 + \cos(m\phi_{ijkl} - \gamma_m)). \tag{17}$$
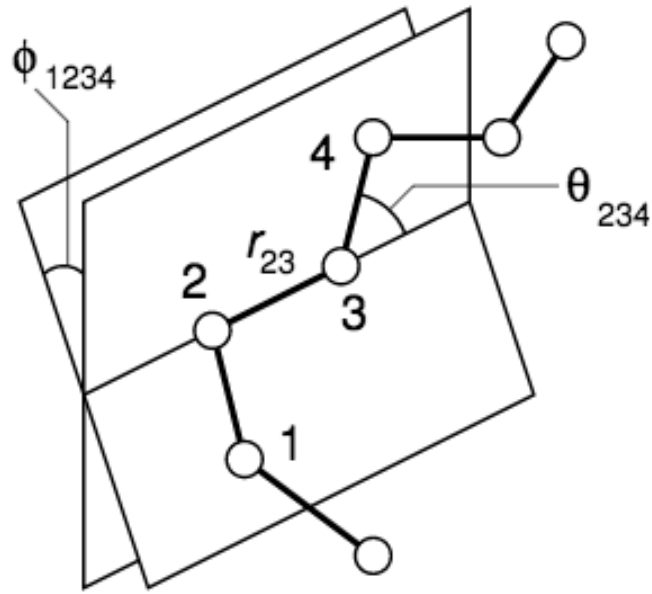
Figure 2 Simple molecular model

Having specified the potential energy function $\mathcal{U}(r^N)$, the atomic forces can be calculated as

$$f_i = \frac{\partial}{\partial r_i} \mathcal{U}(r^N). \tag{18}$$

Therefore, we can get the atomic momenta $p^N = (p_1, p_2, \dots p_N)$, and the velocities of atoms by the classical equations of motion

$$\dot{r}_i = p_i/m_i \qquad \text{and} \qquad \dot{p}_i = f_i \tag{19}$$

using the Verlet algorithm (finite different method) [14].

In molecular dynamics simulations, small-size sample are used to ensure time efficiency. Thus, unless surface effects are of particular interest, periodic boundary conditions need to be applied.

REASEACH MODEL AND HYPOTHESIS

Previous studies [4] have shown that the thermal conductivity of cement paste is relatively low compared with other materials such as silicon. As studied in details for silicon nanowires, in disordered systems, two combined effects are responsible for its heat transport: propagating vibration modes of phonon, and nonpropagating modes. For vibration modes of lower frequencies, phonons are propagating, carrying heat with their motion. Group velocity can be assigned to these modes. Within the single mode relaxation approximation [15], the contribution (k_i) to k of each phonon mode is given by [5]

$$k_i(q) = C_i(q)v_i{}^2(q)\tau_i(q), \tag{20}$$

where $v_i(q)$ and $\tau_i(q)$ are the group velocities and the relaxation times of phonon modes with momentum q, respectively. $C_i(q)$ is the specific heat per unit volume of each vibrational state, using the Bose-Einstein statistics. This equation may be used to compute the contribution to thermal conductivity only of propagating vibrational modes.
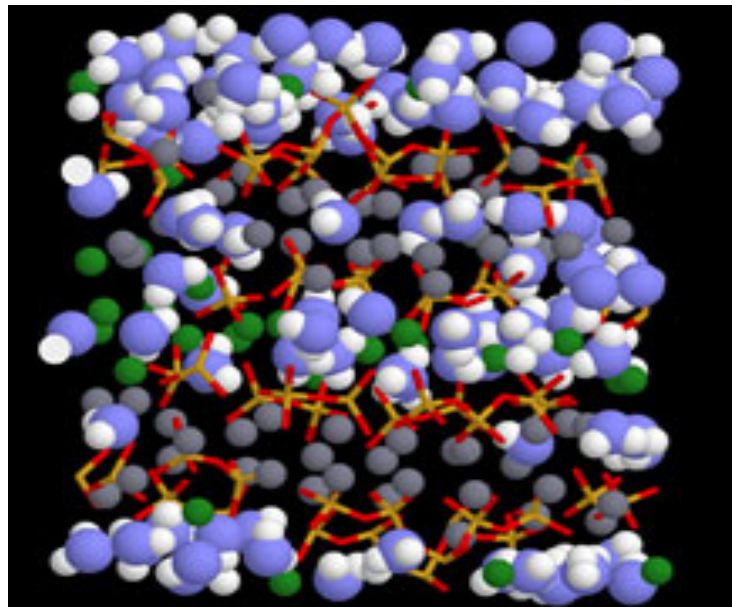

Figure 3 The molecular model of C-S-H: the blue and the white spheres are oxygen and hydrogen atoms of water molecules, respectively; the green and gray spheres

are inter- and intra-layer calcium ions, respectively; yellow and red sticks are silicon and oxygen atoms in silica tetrahedral.

However, unlike crystalline materials, in amorphous materials, nonpropagating modes also contribute to the thermal transport, which should not be neglected. When vibrational frequency reaches the cut-off frequency, group velocity becomes zero. Above this frequency, phonons don't propagate but still are capable of carrying heat. The contribution k_i to k of nonpropagating modes is computed using the AF theory [7], where $k_i = C_i D_i$ and the mode diffusivity is given by

$$D_i = \frac{\pi V^2}{\hbar^2 \omega^2} \sum_{j \neq i} |\langle i|J_z|j\rangle|^2 \delta(\omega_i - \omega_j). \tag{21}$$

Here, $\langle i|J_z|j\rangle$ is the z component of the heat flux operator projected on the i and j vibrational eigenstates.

On the other hand, molecular dynamics (MD) simulations can be performed to study heat transport in bulk systems and nanostructures, in which k is computed through an equilibrium MD approach – Green-Kubo method.

In this study, we will perform a series of MD simulations on C-S-Hs. Since cement paste is an amorphous material, we are going to probe both its propagating and nonpropagating heat transport mechanisms using the equations above. Taking these two effects into consideration, we expect that the thermal conductivity we get from our analytical model should match the results from molecular dynamical simulations.

METHODOLOGY

Molecular dynamical Simulation

Conductive heat transfer can be expressed with Fourier's law

$$J_\mu = -\sum_\nu k_{\mu\nu} \frac{\partial T}{\partial x_\nu}, \tag{22}$$

where J_μ is a component of heat flux, $k_{\mu\nu}$ is an element of the thermal conductivity tensor, and $\frac{\partial T}{\partial x_\nu}$ is the temperature gradient. In experiment, thermal conductivity can be obtained by measuring the temperature gradient that results from the application of a heat current. In MD simulations, the thermal conductivity can be computed either using nonequilibrium MD or equilibrium MD [16]. Direct method and the Green-Kubo Method are two common ways to compute thermal conductivity.

1) Direct Method

The direct method is a nonequlibrium MD method that imposes a temperature gradient in the simulation box, which is analog to doing an experimental measurement. Figure 4 shows a periodic simulation cell with a temperature gradient generated by a heat source and a heat sink to calculate k. There are two common ways to measure thermal conductivity using the direct method. The first way is to hold the heat source and heat sink at different temperatures to set up two thermostatted regions. In each MD step we tally the energy added to the hot region $\Delta\varepsilon_h$ and the energy subtracted from the cold region $\Delta\varepsilon_c$. The thermal conductivity of the material can be expressed as $k = \frac{(\Delta\varepsilon_h + \Delta\varepsilon_c)/2}{2At\frac{dT}{dz}}$, where $\frac{dT}{dz}$ is temperature gradient. Another method is to add/subtract specified amounts of energy $\Delta\varepsilon$ every time step to both regions. Thus, when the system achieves steady state, the thermal conductivity is given by $k = \frac{\Delta\varepsilon}{2At\frac{dT}{dz}}$.
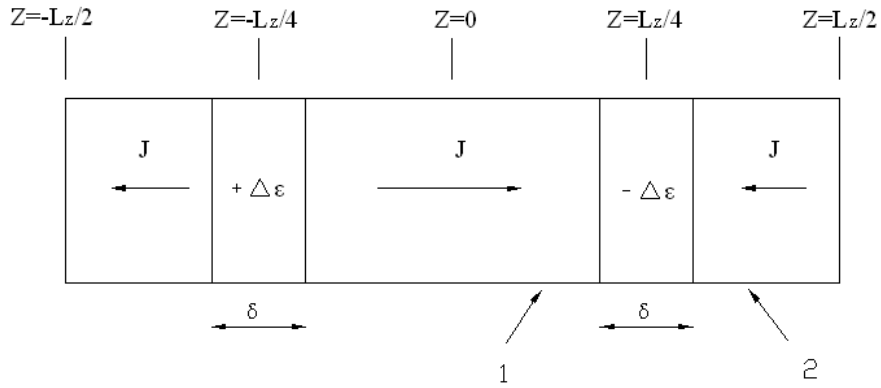
Figure 4 Schematic representation of periodic simulation cell with temperature gradient introduced by a heat source and a heat sink.

The reliability of the direct method depends heavily on the accuracy of the temperature gradient and the Fourier's law. However, if the temperature gradient is too large, significant nonlinearity will be introduced such that Fourier's law no longer applies. Therefore, one should be very careful in choosing the value of $\Delta\varepsilon$ to ensure that the degree of nonlinearity is acceptable. Besides, there is strong nonlinearity of the temperature profile near the heat source and sink, which should be neglected when calculating the temperature gradient.

For a system with length smaller than the phonon mean-free path, finite-size effect becomes significant, which limits its thermal conductivity. This results from the scattering at the interfaces with the heat source and sink. It has been shown [16] that $\frac{1}{k}$ and $\frac{1}{L_z}$ are linearly related. Therefore, the thermal conductivity of an infinite system can be obtained by an extrapolation of the results of a series of different dimensions to an infinite-size system, as shown in Fig. 5.

2) Green-Kubo Method

In our study, we choose Green-Kubo method to calculate the thermal conductivity of CSH.

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Green-Kubo approach is an equilibrium MD method that uses current fluctuations to compute the thermal conductivity via the fluctuation theorem. k could thus be expressed as integration of autocorrelation of heat flux multiplied by a prefactor

$$k_{\mu\nu} = \frac{1}{Vk_BT^2} \int_0^{\tau_m} <J_\mu(\tau)J_\nu(0)> dt, \tag{23}$$

where V is the system volume, k_B is the Boltzmann constant, T is the temperature. Since Green-Kubo method is based on equilibrium, and no driving force is applied to the system, the system is always having a linear response.
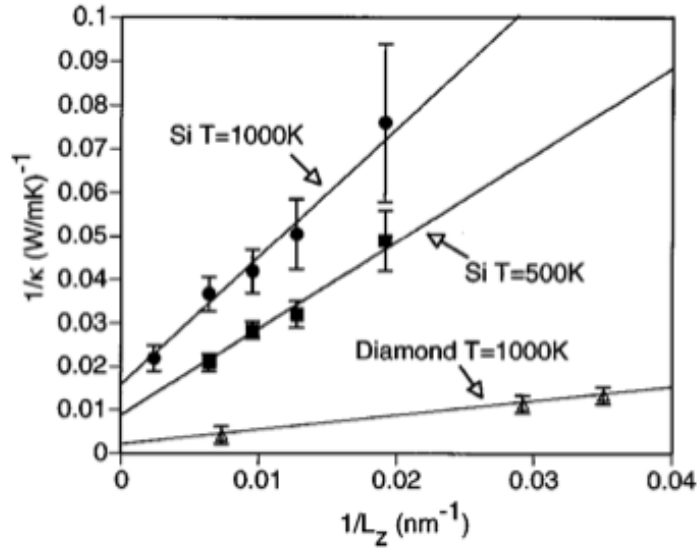

Figure 5 Extrapolation of $1/k$ vs. $1/L$ plots from finite size simulation boxes to infinite large boxes for silicon at 1000K, 500K, and Diamond at 1000K.

To calculate the thermal conductivity of CSH, we apply periodic boundary condition in all directions and set the MD step of Δt. Initially all CSH samples are relaxed in isothermal – isobaric ensemble (NPT) and canonical (NVT) ensembles at 300 K and 0 atm. Then a micro canonical ensemble (NVE) is set to ensure no impact from external forces for the calculation of the heat flux along the MD trajectory. To make our results more statistically reliable, several independent simulations are

performed. To compute the thermal conductivity using the heat current obtained via NVE ensemble simulation, Eq. (23) becomes

$$k_{\mu\nu}(\tau_M) = \frac{1}{Vk_BT^2} \sum_{m=1}^{M} (N-m)^{-1} \sum_{n=1}^{N-m} J_\mu(m+n)J_\nu(n), \qquad (24)$$

where $\tau_M = M\Delta t$, $J_\nu(n)$ is the νth component of heat current at time step n.

Analytical method

1) BTE equation

Bose–Einstein statistics describes the statistical behavior of non-interacting indistinguishable particles that occupy a set of available discrete energy states at thermodynamic equilibrium. Under the single mode relaxation time approximation [15], the BTE method gives a simple expression [5] for thermal conductivity of mode i

$$k_i(\boldsymbol{q}) = C_i(\boldsymbol{q})v_i{}^2(\boldsymbol{q})\tau_i(\boldsymbol{q}), \qquad (25)$$

where $v_i(\boldsymbol{q})$ and $\tau_i(\boldsymbol{q})$ are the group velocity and relaxation time (lifetime) of the phonon eigen mode i with momentum $\boldsymbol{q}$, respectively. $C_i(\boldsymbol{q})$ is the specific heat per unit volume of each vibration state. This equation allows us to analyze the contribution of thermal conductivity from each eigen modes to the total thermal conductivity of a material.

In order to get the thermal conductivity using BTE equation, $C_i(\boldsymbol{q})$, $v_i(\boldsymbol{q})$ and $\tau_i(\boldsymbol{q})$ should be obtained for each phonon mode i.

a. Group velocity

Group velocity of a wave is the velocity with which the overall shape of the waves' amplitudes propagates through space. The group velocity of phonon is given by the slope of the phonon dispersion relation

$$v_g = \frac{d\omega}{dk}, \qquad (26)$$

where ω is the wave's angular frequency, and k is the angular wave number.

Here, we compute the group velocity by performing a central difference on Eq. (26) using close-space wave vectors. Gulp is a program for performing simulations on

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materials using lattice dynamics [17]. By doing phonon calculations of C-S-H in GULP, we can get phonon frequencies for different k points. In our calculation, we set 10 k points very close to the gamma point in each of the four directions, (1, 0, 0), (0, 1, 0), (0, 0, 1) and (1, 1, 1) respectively. The dispersion relation around gamma point can be obtained for each direction, from which we can get the group velocity of each direction.

b. Phonon Relaxation time (Phonon lifetime)

For a simulation box with N atoms, each atom has one longitudinal and two transverse phonon modes associated with it. This leads to 3N phonon modes. A. J. H. McGaughey et al. [18] present a method in which the relaxation time of the ith mode can be obtained by considering the total energy of each mode, $E_i(t)$.

The shape mode of a system can be expressed as

$$S_i(\boldsymbol{\kappa}, \nu) = N^{-1/2} \sum_j M_j^{1/2} exp(-i\,\boldsymbol{\kappa}\cdot\boldsymbol{r}_{j,0})e_i^*(\boldsymbol{\kappa}, \nu)\cdot\boldsymbol{u}_j\,, \qquad (27)$$

where M_j is the mass, $\boldsymbol{r}_{j,0}$ is the equilibrium position, and $\boldsymbol{u}_j$ is the displacement of atom j, respectively. N is the number of atoms, and $e_i^*(\boldsymbol{\kappa}, \nu)$ is the complex conjugate of the eigenvector of wave vector $\boldsymbol{\kappa}$. We do our calculation at gamma point, so $\boldsymbol{\kappa}$ becomes (0, 0, 0). Therefore, the exponential term becomes 1 and Eq. (27) can be simplified as

$$S_i(\boldsymbol{\kappa}, \nu) = N^{-1/2} \sum_j M_j^{1/2} \cdot e_i^*(\boldsymbol{\kappa}, \nu)\cdot\boldsymbol{u}_j. \qquad (28)$$

The total energy of each mode i can be given by

$$E_i(t) = \omega_i^2 S_i^* S_i \big/ 2 + \dot{S}_i^* \dot{S}_i \big/ 2, \qquad (29)$$

where the first term is the potential energy, and the second term is the kinetic energy. The temporal decay of the autocorrelation of $E_i(t)$ is related to the relaxation time of that mode. The relaxation time is obtained by fitting the data with an exponential decay.

From GULP phonon calculation, eigenfrequencies ω_i and the corresponding eigenvectors of phonon vibration can be obtained. The displacements of atoms at time t are given by the MD simulations.

2) AF theory

The contribution to the total thermal conductivity from phonon modes with zero group velocity becomes zero according to BTE equation. BTE results are however substantially smaller than MD values for many cases [. In disordered system, most of the vibrational modes do not have a well-defined polarization and cannot be properly assigned a group velocity. Although these modes do not propagate as phonons in crystals, they may have diffusivity such that they can still carry heat. Participation ratio is a way to quantify the fraction of atoms participating in a given vibrational mode. It's defined as

$$p_i^{-1} = N \sum_n \left[\sum_\alpha e_{\alpha,n}^*(i) e_{\alpha,n}(i) \right]^2, \tag{30}$$

where $e_{\alpha,n}(i)$ is the component of the eigenmode i relative to the coordinate α of the atom n. By calculation of the participation ratio of some disordered systems [19], it has been found that modes with zero group velocity do not necessarily localize. To the contrary, localization doesn't happen until very high vibration frequencies.

AF theory was first proposed by Allen and Feldman in 1993 [7]. The theory describes the contribution from non-propagating states to the thermal conductivity of a disordered system, where $k_i = C_i D_i$, and the mode diffusivity is given by

$$D_i = \frac{\pi V^2}{\hbar^2 \omega_i^2} \sum_{j \neq i} |\langle i | J_z | j \rangle|^2 \, \delta(\omega_i - \omega_j). \tag{31}$$

Here, $\langle i | J_z | j \rangle$ is the z component of the heat flux operator projected on the i and j vibrational eigen states. From our group velocity calculation, we can get the cut-off frequency above which the group velocity of the system becomes zero. For vibrational phonon frequencies higher than the cut-off frequency, modes have diffusivity thus providing a substantial contribution to thermal transport.

In order to quantitatively model the thermal conductivity of C-S-Hs, we have treated the propagating phonon modes up to its cut-off frequency by using the BTE, while we employed Eq. (31) to compute the contribution to of diffusive modes.

RESULTS AND DISCUSSION

MD simulations

Here we perform the MD Green-Kubo simulation on a 501-atom CSH simulation box with periodic boundary condition. The time step is set to be $\Delta t = 0.1$fs. To ensure statistical reliability, 7 independent simulations are performed, each 10^7 steps long. Fig.6 shows the thermal conductivity and normalized autocorrelation of heat flux for the 7 MD simulations. As shown in the figure, the system reaches equilibrium after 5000fs. From Fig.6(a), we get the thermal conductivity of CSH $k = 1.685$ W/mK, by averaging all the thermal conductivities for the 7 samples after $t = 5\times10^3$ fs.

GULP analysis

Phonon analyses are performed in GULP, from which we can get the group velocity, participation ratio, relaxation time, and the mode diffusivity.

1) Group velocity

Based on the method in the previous chapter, we use finite difference method to compute the group velocity of CSH. 10 close-spaced k points near gamma point are picked for [1, 0, 0], [0, 1, 0], [0, 0, 1] and [1, 1, 1] directions, respectively, with interval of 0.003 (Shown in Table 1). For each direction, we get 1503 sets of data with 10 points, corresponding to 1503 eigen modes. By linear line fitting, we obtain 1503 slopes, which correspond to group velocities of the 1503 eigen modes. By averaging group velocities from all the four directions for each mode, we get the mean group velocity for CSH, as shown in Fig.7.

The group velocities of the C-S-H system varnish as the vibrational frequency increases. It goes to zero around frequency of 1000 cm^{-1}. The group velocities at 1500 cm^{-1} and 3700 cm^{-1} are due to the vibrations for H-O-H bonds in water, and
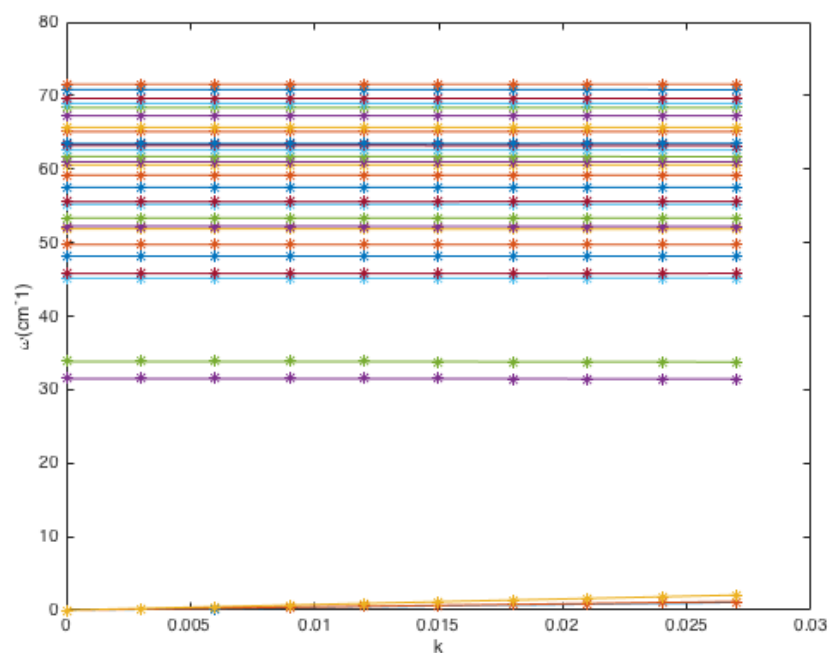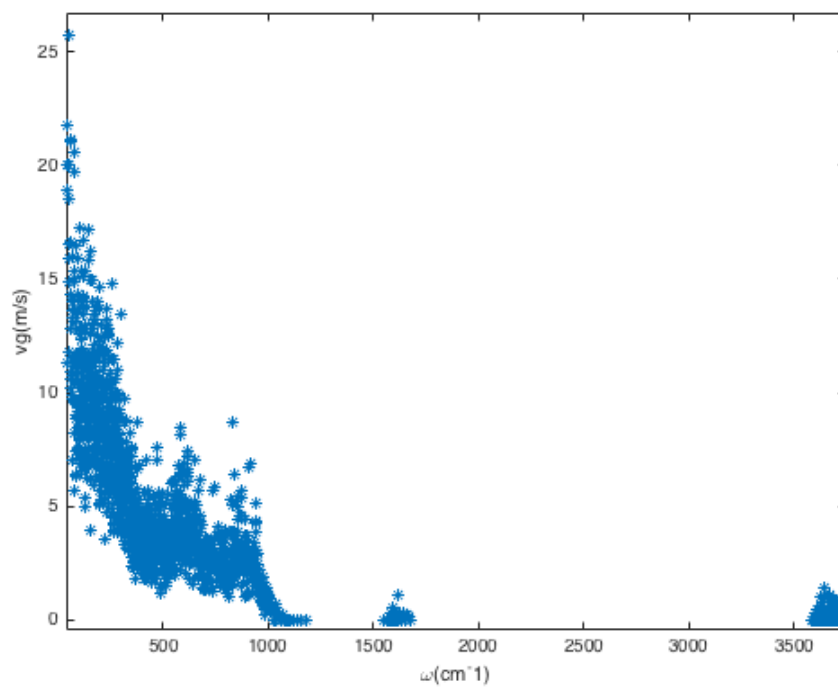
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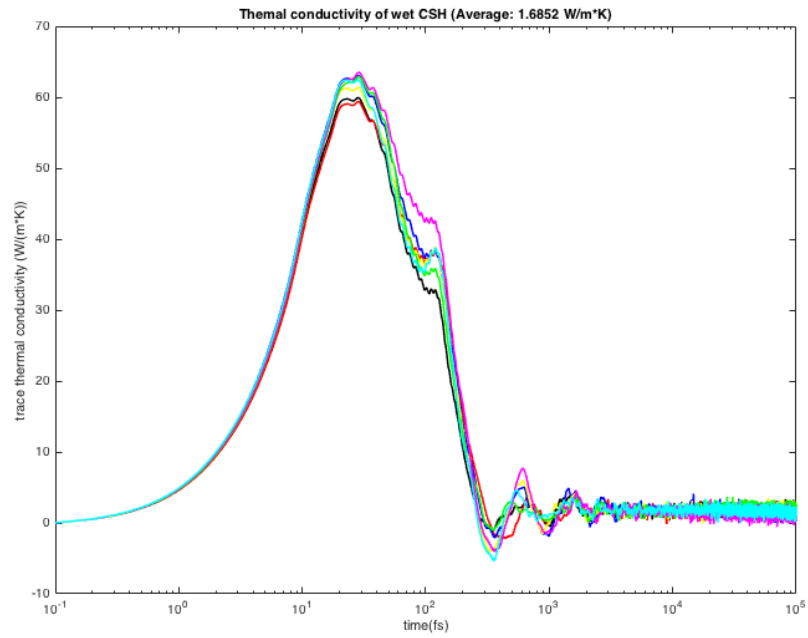
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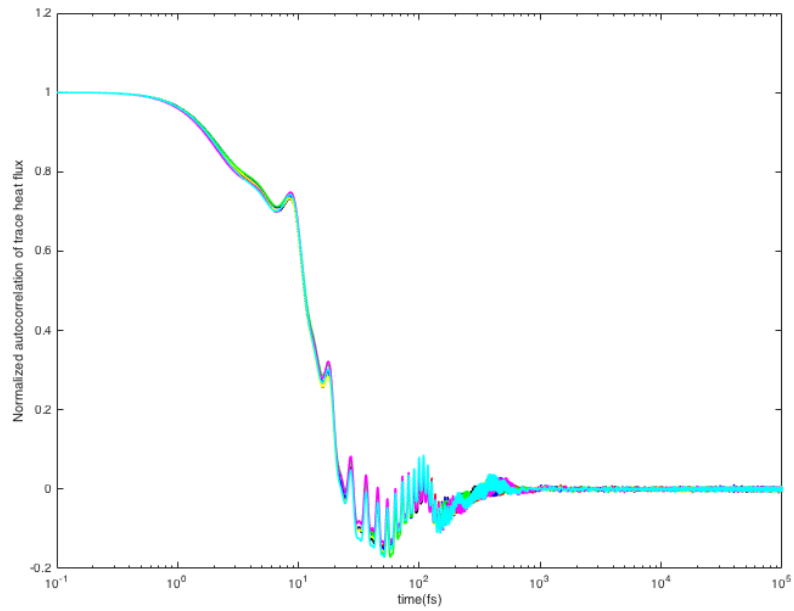
(b)

Figure 6 (a) Thermal conductivity and (b) the normalized autocorrelation of heat flux of 7 independent CSH simulation samples ($\tau_M = 10^6$ fs).

(a)

(b)

Figure 7 (a) Linear fittings of the first 30 dispersion curves of the C-S-H near gamma point in the [0, 0, 1] direction, and (b) the group velocities of the vibrational modes.

Table 1: Values of k points used in group velocity calculations.

Directions	[1, 0, 0]	[0, 1, 0]	[0, 0, 1]	[1, 1, 1]
1	[0, 0, 0]	[0, 0, 0]	[0, 0, 0]	[0, 0, 0]
2	[0.003, 0, 0]	[0, 0.003, 0]	[0, 0, 0.003]	[0.003, 0.003, 0.003]
3	[0.006, 0, 0]	[0, 0.006, 0]	[0, 0, 0.006]	[0.006, 0.006, 0.006]
4	[0.009 0, 0]	[0, 0.009, 0]	[0, 0, 0.009]	[0.009, 0.009, 0.009]
5	[0.012, 0, 0]	[0, 0.012, 0]	[0, 0, 0.012]	[0.012, 0.012, 0.012]
6	[0.015, 0, 0]	[0, 0.015, 0]	[0, 0, 0.015]	[0.015, 0.015, 0.015]
7	[0.018, 0, 0]	[0, 0.018, 0]	[0, 0, 0.018]	[0.018, 0.018, 0.018]
8	[0.021, 0, 0]	[0, 0.021, 0]	[0, 0, 0.021]	[0.021, 0.021, 0.021]
9	[0.024, 0, 0]	[0, 0.024, 0]	[0, 0, 0.024]	[0.024, 0.024, 0.024]
10	[0.027, 0, 0]	[0, 0.027, 0]	[0, 0, 0.027]	[0.027, 0.027, 0.027]

O-H bonds, respectively. For other vibrational frequencies, no proper group velocity can be assigned.
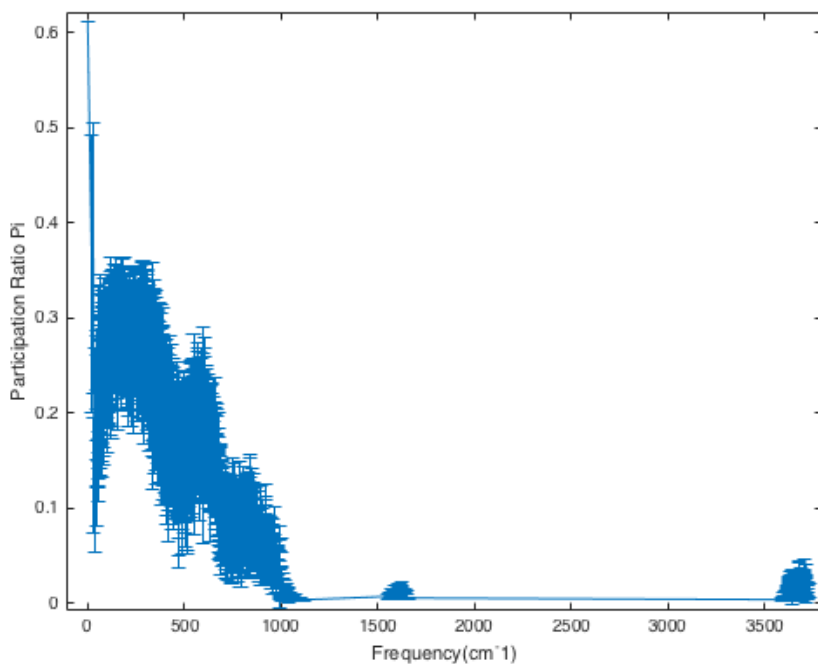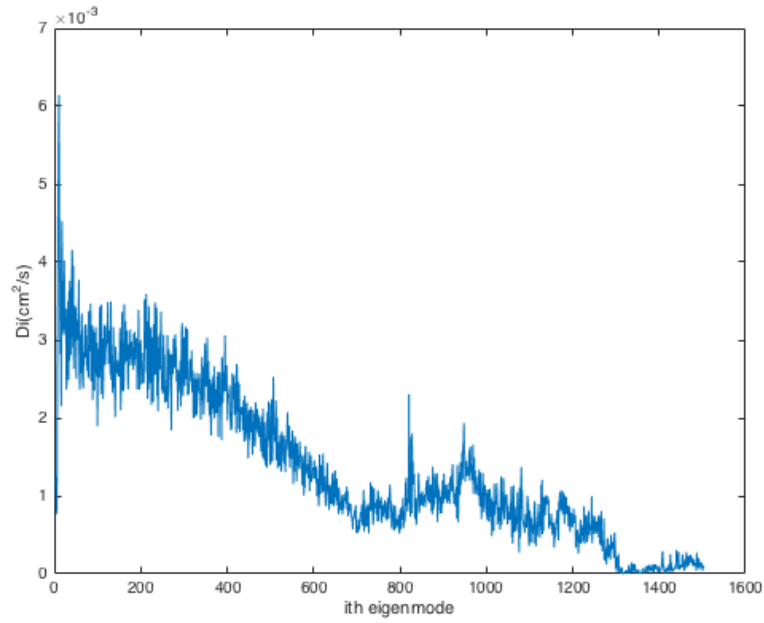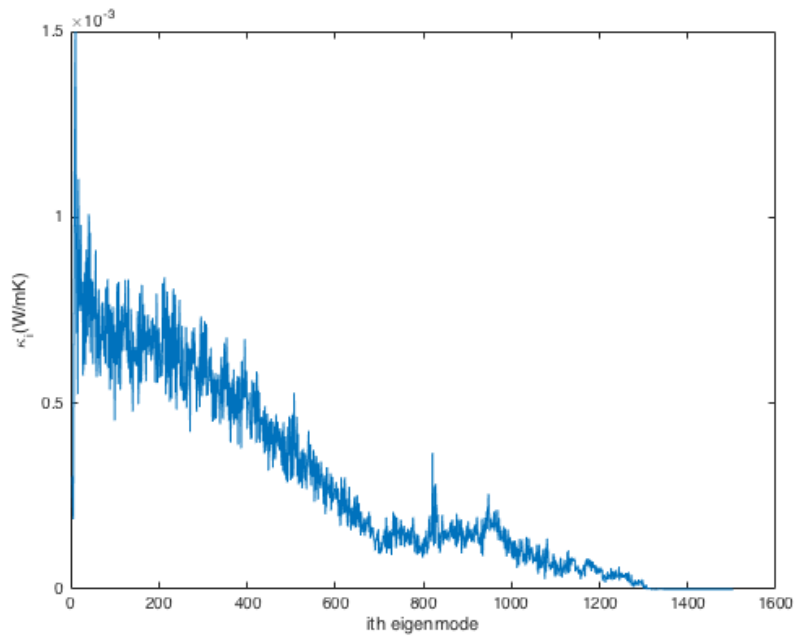

Figure 8 Participation ratios of vibrational modes of CSH.

(a)

(b)

Figure 9 (a) Mode diffusivity of each vibrational mode, and (b) the thermal conductivity coming from the corresponding mode diffusivity.

2) Participation ratio

Fig.8 shows the participation ratios with error bars computed for vibrational modes of CSH. From the figure, we can see that less atoms participate in the vibration of the system when the eigenfrequency increases. For frequencies beyond 1000 cm^{-1}, the system begins to localize. This means that the phonon modes do not propagate and become less active at higher frequencies, where nonpropagting modes may be dominant for its heat transfer.

3) Mode diffusivity

Mode diffusivities for CSHs and the thermal conductivities for each mode calculated from AF theory are obtained using GULP, as shown in Figure 9.

The difference between the thermal conductivity we got from MD simulations, and the thermal conductivity from the mode diffusivity obtained by AF theory, should come from the propagating modes that can be explained by Bose-Einstein transport equation, which satisfies

$$\kappa_{BTE} = \kappa_{MD} - k_{AF}, \tag{32}$$

where k_{BTE} can be obtained by Eq. (25).

Future perspective

Due to time limitation, we haven't finished the calculation of propagating part of thermal conductivity of C-S-Hs. We will continue to conduct research on BTE heat transport of C-S-Hs. Once we get the relaxation time of each phonon vibrational mode, we will be able to calculate the k_{BTE} by Eq. (25). We will calculate the ratio

$$R = \frac{\kappa_{BTE}}{k_{AF}}. \tag{33}$$

We are expecting to see a sudden transition in the value of R at a certain frequency. We set this frequency to be the boundary frequency ϖ_{cutoff} for propagating modes and nonpropagating modes in C-S-H. Vibraional frequencies higher than ϖ_{cutoff} will be treated as propagating modes, while modes of lower frequencies will be considered as nonpropagating modes. The summation of thermal conductivities from these two modes is expected to be equal to the thermal conductivity from MD Green-Kubo simulations.

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