Predicting Vibrational Mean Free Paths in Disordered Systems

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Abstract

The thermal conductivity of a dielectric or semiconducting material can be predicted using the phonon frequencies and lifetimes. Techniques for predicting these properties have been proposed based in molecular dynamics simulation, lattice dynamics calculations, and the phonon spectral energy density. Here, two expressions for the phonon spectral energy density are described and applied to three test systems: Lennard-Jones argon, Stillinger-Weber silicon, and carbon nanotubes modeled using the REBO potential. One phonon spectral energy density expression is derived from lattice dynamics theory, while the other uses only the atomic velocities from molecular dynamics simulation. We find that while the phonon spectral energy density that only uses atomic velocities can predict the phonon frequencies, it does not correctly predict the lifetimes.

I. INTRODUCTION

Measurements by Moon. Measurements by all the refs from Galli paper. The key to understanding such measurement is to estimate a MFP for the vibrational modes in disordered systems.

The goal of this work is to predict the MFP of vibrational modes in disordered systems. Simple Lennard-Jones systems will be studied. A perfect LJ crystal are alloyed with a species of differing mass and amorphous samples are prepared. The vibrational modes in these systems are characterized in the limit of propagating (phonon) and non-propagating (diffuson) modes by predicting the mode lifetimes and estimating their mean free paths. Estimating an effective dispersion relation is necessary for calculating an effective group velocity for disordered, which is crucial for transforming lifetimes to MFPs. The spectrum of phonon MFPs and the accumulated thermal conductivity are predicted for a model of amorphous silicon. Predictions of thermal conductivity using a boundary scattering model demonstrates

Ref Cahill paper, vg=vs. Ref Galli paper, its unclear what the group velocity should be.[1]

II. LIFETIMES AND MFPS OF VIBRATIONAL MODES

Previous studies[1].

A. Normal Mode Decomposition

Discuss normal mode decomposition and its limitations.[2]
Discuss why real-space method is necessary in this case.

B. Lifetimes of Disordered Vibrational Modes

If determine by Ioffe-Regel limit, $\tau\binom{\kappa}{\nu} < 1/\omega\binom{\kappa}{\nu}$, Figure .

III. CHARACTERIZATION

Determine by mean free path condition:

$\Lambda > \lambda$

Requires a

IV. EFFECTIVE VELOCITIES OF VIBRATIONAL MODES

It is difficult to assign a wavevector (and hence a wavelength) to disordered mode. There-fore, some limit must be imposed:

$\Lambda > a$

Where a is the lattice spacing.

V. ORDERED ALLOYS

A. Phonon Dispersion

- $v_g(m_r)$

- two masses with $v_g(m_r)$, maybe compare with 4 masses with higher mass ratio.

- Keep m_{avg} constant for all.

- run a system with a "softer" and "stiffer" LJ (smaller/bigger eps or sigma). This can be used as a comparison for the phonon/diffuson spectrums which will be shown later.

B. Phonon Lifetimes

- compare lifetimes from 2 atom alloy, 4 atom alloy. Is the reduction in thermal conduc-tivity mostly due to the reduction in group velocities/introduction of optical modes?

VI. DISORDERED ALLOYS

A. Effective Phonon Dispersion

- compare versus virtual crystal

B. Effective Phonon Lifetimes

- compare c=0.0,0.05,0.15

- why not bond disorder? This has been investigated such as in Schelling Si/Ge[?] , Marzari Si/Ge PRL[?] . Although, detailed study of PbTe/PbSe systems (Esfarjani/Shiomi preprint) demonstrate the importance of bond environment for alloys.

- if consider bond disorder, pick a "softer/stiffer" system. This system should be less/more sensitive to alloying which is discussed later. Could reference the PbTe/PbSe paper about this.

- compare these predicted lifetimes to predictions from:

$$\frac{1}{\tau_{mass}} = \frac{\pi}{2N}\omega^2\left(\begin{smallmatrix}\boldsymbol{\kappa}\\\nu\end{smallmatrix}\right)\sum_{\boldsymbol{\kappa}',\nu'}^{N,3n}\delta\left(\omega\left(\begin{smallmatrix}\boldsymbol{\kappa}\\\nu\end{smallmatrix}\right)-\omega\left(\begin{smallmatrix}\boldsymbol{\kappa}'\\\nu'\end{smallmatrix}\right)\right)\sum_b^n g(b)|e^*\left(\begin{smallmatrix}\boldsymbol{\kappa}\ b\\\nu\ \alpha\end{smallmatrix}\right)\dot{e}\left(\begin{smallmatrix}\boldsymbol{\kappa}\ b\\\nu\ \alpha\end{smallmatrix}\right)|^2, \tag{1}$$

$g(b) = \sum_i f_i(b)[1 - m_i(b)/m_{avg}(b)]^2$

C. Disappearance of SED Peaks

- show SED plot of mode peaks from c=0.0,0.05,0.15,0.5 for any mode where a peak still shows in 0.5

D. Propagating Modes in Heavily Disordered Alloys

- Analysis of c=0.5 modes at gamma, which modes are plane-wave like?

VII. HEAT TRANSPORT IN AMORPHOUS SYSTEM

A. Effective Phonon Dispersion

- compare predicted sound speeds from finite dispersion acoustic branch (dk pi/100L), bulk modulus

B. Allen Feldman Diffuson Theory

- thermal transport in terms of a diffusivity, no need for a propagation velocity

C. Diffuson Lifetimes

- measured using NMD and anharmonic MD.

- extract effective Diffuson velocity, compare to sound speed

- use sound speed to predict a phonon MFP, establish a MFP cut-off criteria to call something a phonon or not. Could be MFP ¿ lattice constant or something. However, there are no wavelengths (yet).

D. Propagating Modes in Amorphous System

- Analysis of c=0.5 modes at gamma, which modes are plane-wave like? This will be the key to the length scale needed to compare with the MFP predicted above. The plane-wave like modes will be identified by fourier transforming the eigvec. It should show content at a small number of wavevectors, and 1 should be dominant and of the order of pi/L.

E. Role of Anharmonicity in Disordered Thermal Transport

- run harmoninc FC MD, predict thermal conductivity using GK

- compare anharmonic GK, harmonic GK, and AF predictions. May possibly need to run "stiffer" system to compare with $k_{si} = k_{ph} + kAF = 0.5 + 0.5$.

VIII. THERMAL DIFFUSIVITY IN ORDERED AND DISORDERED SYSTEMS

- plot AF and phonon diffusivities for all systems above.

- Show that for high mass ratio ordered alloys and disordered alloys, the thermal diffusivities are on the order of amorphous system.

- For high mass ratio ordered alloys, it is the reduction of the group velocities through decreased acoustic and introduced optical branches.

- For the disordered alloys, the phonon lifetimes of high frequency modes are drastically reduced as alloy concentration is increased. Should show that this effect is less drastic for "soft" (soft bond) or "acoustically" matched systems (low mass ratio). It is more drastic for large acoustically mismatched systems (high mass ratio) or stiff systems.

- For amorphous systems, there is not a unique choice of the phonon MFP. Instead, it is helpful to consider the diffusons and their thermal diffusitivty. Compared to high mass ratio ordered alloys and heavily disordered alloys, these thermal diffusivities are comparable.

- Compare high mass ratio ordered alloys optical branch group velocities/lifetimes (diffusivities) to amorphous diffusivities ("group velocity" and "lifetime"). Are they really distinguishable?

A.   Limits of the AF Diffusivity

It was noticed by Birch and Clark (1940), and by Kit- tel (1948) that in glasses (T) at T ¿20K could be in- terpreted as the specific heat $C(T)/V$ multiplied by a temperature-independent diffusivity D of order a2 D /3 where a is an interatomic distance. In the phonon-gas model, this would correspond to l a, too small to jus- tify use of the model. The success of this observation implies that the dominant normal modes in a glass are of the D variety, not P because P implies l a, and not L because L implies $D = 0$ until anharmonic corrections are added which make D depend on T . This successful (and we believe, essentially correct) interpretation lost favor after Anderson localization was understood, because a misconception arose that the P/D boundary (which cer- tainly lies low in the spectrum of a glass) should lie close to the E/L boundary.

Limits of D(w)

/home/jason/Downloads/papers/disorder/PhysRevB.43.6573.pdf

/home/jason/Downloads/papers/disorder/9907132.pdf

Defintions of Fourier Weights

DSF   /home/jason/Downloads/papers/disorder/PhysRevB.59.3551.pdf   Fourier   Mode Weights /home/jason/Downloads/papers/disorder/PhysRevLett.60.2280.pdf

B. Thermoelectric Energy Conversion using Large Unit Cell Skutterudites

Appendix A: Predicting Phonon Properties

1. Vibrations in Ordered Solids

In a crystal (periodic) system, the vibrations of atoms are described by a basis of eigenfunctions called phonon normal modes, which are determined by the properties of the crystal (see Appendix A 3). The eigenvalues of this basis are the phonon mode frequencies (energies).[?][?] The atomic velocities can be represented by the velocity normal mode coordinate, defined as[?]

$$\dot{u}_\alpha(^l_b;t) = \sum_{\boldsymbol{\kappa}',\nu}^{N,3n} \frac{1}{\sqrt{m_b N}} \exp\left[i\boldsymbol{\kappa}' \cdot \mathbf{r}_0(^l_0)\right] e^*(^{\boldsymbol{\kappa}\ b}_{\nu\ \alpha}) \dot{q}(^{\boldsymbol{\kappa}}_\nu;t). \tag{A1}$$

Here, $\dot{q}(^{\boldsymbol{\kappa}}_\nu;t)$ represents the kinetic energy $T(^{\boldsymbol{\kappa}}_\nu;t)$ of the mode with phonon frequency $\omega_0(^{\boldsymbol{\kappa}}_\nu)$ by[?]

$$T(^{\boldsymbol{\kappa}}_\nu;t) = \frac{\dot{q}^*(^{\boldsymbol{\kappa}}_\nu;t)\,\dot{q}(^{\boldsymbol{\kappa}}_\nu;t)}{2}. \tag{A2}$$

The phonon mode kinetic energies $T(^{\boldsymbol{\kappa}}_\nu;t)$ are used to calculate the phonon spectral energy denisty in Appendix A 2.

2. Predicting Phonon Lifetimes using Spectral Energy Denisty

The phonon normal mode coordinate is,

$$\dot{q}(^{\boldsymbol{\kappa}}_\nu;t) = \sum_{\alpha,b,l}^{3,n,N} \sqrt{\frac{m_b}{N}}\, \dot{u}_\alpha(^l_b;t)\, e^*(^{\boldsymbol{\kappa}\ b}_{\nu\ \alpha}) \exp[i\boldsymbol{\kappa} \cdot \mathbf{r}_0(^l_0)], \tag{A3}$$

which form the basis for vibrations in ordered materials and represents the phonon mode kinetic energy. The normal mode kinetic energy can be transformed from the time domain t to the frequency domain ω by Parseval's theorem,[?]

$$T(^{\boldsymbol{\kappa}}_\nu;\omega) = \lim_{\tau_0 \to \infty} \frac{1}{2\tau_0} \left| \frac{1}{\sqrt{2\pi}} \int_0^{\tau_0} \dot{q}(^{\boldsymbol{\kappa}}_\nu;t) \exp(-i\omega t)dt \right|^2. \tag{A4}$$

Here, $T(^{\boldsymbol{\kappa}}_\nu;\omega)$ represents the spectral energy of the phonon normal mode with frequency $\omega(^{\boldsymbol{\kappa}}_\nu;\omega)$. Following the derivation in Appendix C, one arrives at the expression for the SED

FIG. 1: The SED (Φ) for the first three polarizations at the wavevector $[\pi/4a, \pi/4a, \pi/4a]$ for LJ argon at a temperature of 20 K. There are two degenerate transverse acoustic polarizations and one longitudinal acoustic polarization (of higher frequency).[?] When fitting the SED, the different polarizations can be fit individually using single Lorentzian peaks or as a superposition of peaks. Here the two peaks are fit individually with Φ plotted as a superposition. The predicted lifetimes of these polarizations, which are inversely proportional to the peak widths Γ, are provided in the legend.

of a single phonon mode,

$$T(^{\boldsymbol{\kappa}}_{\nu}; \omega) = \frac{C_0(^{\boldsymbol{\kappa}}_{\nu})}{2} \frac{\Gamma(^{\boldsymbol{\kappa}}_{\nu})/\pi}{[\omega_0(^{\boldsymbol{\kappa}}_{\nu}) - \omega]^2 + \Gamma^2(^{\boldsymbol{\kappa}}_{\nu})}, \tag{A5}$$

which is a Lorentzian function with center at $\omega_0(^{\boldsymbol{\kappa}}_{\nu})$ and a half-width at half-maximum (linewidth) of $\Gamma(^{\boldsymbol{\kappa}}_{\nu})$ and $C_0(^{\boldsymbol{\kappa}}_{\nu})$ is a constant. We know from anharmonic lattice dynamics theory that the phonon linewidth is related to the phonon lifetime, $\tau(^{\boldsymbol{\kappa}}_{\nu})$, by[? ?]

$$\tau(^{\boldsymbol{\kappa}}_{\nu}) = \frac{1}{2\Gamma(^{\boldsymbol{\kappa}}_{\nu})}. \tag{A6}$$

The MD simulations we perform here are classical. For a classical system in the harmonic limit (i.e., temperature approaching zero) there is an equipartition of energy and $\sum_{\nu}^{3n} T(^{\boldsymbol{\kappa}}_{\nu}; \omega) = \sum_{\nu}^{3n} V(^{\boldsymbol{\kappa}}_{\nu}; \omega)$.[?] In an anharmonic system (i.e., a MD simulation), the assumption of equipartition of energy can be tested by predicting the system-level specific heat. By assuming equipartition of energy, the phonon SED at a particular wavevector is

$$\Phi(\boldsymbol{\kappa}, \omega) = 2 \sum_{\nu}^{3n} T(^{\boldsymbol{\kappa}}_{\nu}; \omega) = \sum_{\nu}^{3n} C_0(^{\boldsymbol{\kappa}}_{\nu}) \frac{\Gamma(^{\boldsymbol{\kappa}}_{\nu})/\pi}{[\omega_0(^{\boldsymbol{\kappa}}_{\nu}) - \omega]^2 + \Gamma^2(^{\boldsymbol{\kappa}}_{\nu})}, \tag{A7}$$

which is a superposition of $3n$ Lorentzian functions with centers at $\omega_0(^{\boldsymbol{\kappa}}_{\nu})$ (one for each polarization). For simplicity, we refer to $\Phi(\boldsymbol{\kappa}, \omega)$ as Φ. Given a set of atomic velocities, Φ can be calculated using Eq. (C3) and (C12), and then fit using Eq. (C15) to extract the phonon properties $\omega_0(^{\boldsymbol{\kappa}}_{\nu})$ and $\tau(^{\boldsymbol{\kappa}}_{\nu})$.

3. Allowed Wavevectors in Ordered Systems

The phonon spectral energy is defined for the allowed wavevectors of a crystal, which can be specified from the crystal structure's Bravais lattice and its basis, i.e. unit cell. A

D-dimensional Bravais lattice is a collection of points with positions

$$\mathbf{u}_0\binom{l}{0} = \sum_{\alpha}^{D} N_\alpha \mathbf{a}_\alpha \qquad (A8)$$

where N_α and the summations if over the lattice vectors, $\mathbf{a}_\alpha$.[?] The basis (or unit cell) is the building block of the crystal and they are arranged on the points defined by the Bravais lattice. The equillibrium position of any atom in the crystal can be described by

$$\mathbf{u}_0\binom{l}{b} = \mathbf{u}_0\binom{l}{0} + \mathbf{u}_0\binom{0}{b} \qquad (A9)$$

where $\mathbf{u}_0\binom{l}{0}$ is the equilibrium position of the lth unit cell and $\mathbf{u}_0\binom{0}{b}$ is the equilibrium position of the and b^{th} atom in the unit cell relative to $\mathbf{u}_0\binom{l}{0}$. For the LJ systems studied here, the cubic conventional cells are used with four atoms per unit cell.[?] For our MD simulations, cubic simulation domains with periodic boundary conditions are used with $N_1 = N_2 = N_3 = N_0$.[?][?] The allowed wavevectors for such crystal structures are

$$\boldsymbol{\kappa} = \sum_{\alpha} \mathbf{b}_\alpha \frac{n_\alpha}{N_\alpha}, \qquad (A10)$$

where $\mathbf{b}_\alpha$ are the reciprocal lattice vectors[?] and $-N_\alpha/2 < n_\alpha \le N_\alpha/2$, where n_α are integers and N_α are even integers.[?] The wavevectors are taken to be in the first Brioullin zone.[?]

4. Predicting Spectral Energy Density from Molecular Dynamics Simulations

Once the allowed wavevectors are specified (see Section A 3), the atomic velocities from an MD simulation can be used to calculate Φ. To calculate Φ, Eq. (C12) requires the phonon mode eigenvector, which can be obtained *a priori* using quasi-harmonic lattice dynamics calculations using the finite temperature lattice constant.[?] The phonon frequencies and lifetimes are found by fitting Φ with Lorentzian functions using a non-linear least squares method. Both of these phonon properties are independent of the Lorentzian peak magnitude. The different polarizations can be fit individually using single Lorentzian peaks or as a superposition of peaks. At the temperatures studied in this work, we find that fitting single or simultaneous peaks results in less than five percent difference in the predicted lifetimes. The error from fitting the Lorentzian functions is between $5-10\%$ in the predicted lifetimes, with the error increasing with increasing temperature.[‡]To illustrate the procedure, Φ was

calculated using Eq. (C12) for LJ argon with $N_0 = 8$ (2048 atoms) and $T = 20$ K. Φ for the three modes of lowest frequency and wavevector $[\pi/4a, \pi/4a, \pi/4a]$ is shown in Fig. 1. The lower frequency peak corresponds to the 2 degenerate transverse acoustic modes, while the higher frequency peak corresponds to the longitudinal acoustic mode.[?]

5. Thermal Conductivity

Once the frequencies and lifetimes of all phonon modes in the Brillouin zone are obtained, the bulk thermal conductivity in direction $\mathbf{n}$, $k_{\mathbf{n}}$, can be calculated from[?]

$$k_{\mathbf{n}} = \sum_{\boldsymbol{\kappa}} \sum_{\nu} c_{ph}\binom{\boldsymbol{\kappa}}{\nu} v_{g,\mathbf{n}}^2\binom{\boldsymbol{\kappa}}{\nu} \tau\binom{\boldsymbol{\kappa}}{\nu}. \tag{A11}$$

Here, c_{ph} is the phonon volumetric specific heat and $v_{g,\mathbf{n}}$ is the component of the group velocity vector in direction $\mathbf{n}$. Since the systems we consider are classical and obey Maxwell-Boltzmann statistics,[?] the specific heat is k_B/V per mode in the harmonic limit where V is the system volume. This approximation is used here and has been shown to be suitable for LJ argon[?] and SW silicon.[?] The group velocity vector is the gradient of the dispersion curves (i.e., $\partial\omega/\partial\boldsymbol{\kappa}$), which can be calculated from the frequencies and wavevectors using finite differences. In this work, the group velocities are calculated using finite difference and quasi-harmonic lattice dynamics because a very small finite difference can be used which reduces the error.[?] To predict a bulk thermal conductivity, it is necessary to perform a finite simulation size scaling procedure as discussed in Appendix B.

Appendix B: Finite Simulation-Size Scaling for Thermal Conductivity

For the LJ argon system studied in Section ??, a finite simulation-size scaling procedure[? ?] is used to compare the thermal conductivity predictions from Φ and Φ' to those from the Green-Kubo method. The scaling procedure is demonstrated in Fig. 2. The thermal conductivity is predicted from Φ or Φ' and MD simulations with $N_0 = 4, 6, 8$, and 10. The bulk conductivity, k_∞, is then estimated by fitting the data to

$$1/k = 1/k_\infty + A/N_0, \tag{B1}$$

where A is a constant. This procedure is necessary because the first Brillouin zone is only sampled at a finite number of points for a finite simulation size, with no contribution from

FIG. 2: Thermal conductivity predictions for LJ argon calculated using phonon lifetimes predicted by Φ and Φ'.[?] (a) The finite simulation-size scaling extrapolation[? ?] is used to compare the results to bulk predictions made using the Green-Kubo method. (b) The bulk results for Φ and Green-Kubo are in good agreement temperatures of 20 and 40 K with those of other atomistic simulation methods.[?]

the volume at its center. To predict a bulk thermal conductivity, it is important to sample points near the Brillouin zone center, where the modes can have large lifetimes and group velocities.[? ?]

Appendix C: Derivation of Phonon Spectral Energy Density

To derive the phonon Spectral Energy Density, Φ, we begin with harmonic lattice dynamics theory.[? ?] In reciprocal space, the system Hamiltonian, H, is

$$
\begin{aligned}
H =& \frac{1}{2} \sum_{\boldsymbol{\kappa},\nu}^{N,3n} \left[\dot{q}^*(\tfrac{\boldsymbol{\kappa}}{\nu};t)\,\dot{q}(\tfrac{\boldsymbol{\kappa}}{\nu};t) + \omega_0^2(\tfrac{\boldsymbol{\kappa}}{\nu})\,q^*(\tfrac{\boldsymbol{\kappa}}{\nu};t)\,q(\tfrac{\boldsymbol{\kappa}}{\nu};t) \right] \\
=& \sum_{\boldsymbol{\kappa},\nu}^{N,3n} \left[T(\tfrac{\boldsymbol{\kappa}}{\nu};t) + V(\tfrac{\boldsymbol{\kappa}}{\nu};t) \right],
\end{aligned}
\tag{C1}
$$

where t is time, $\omega_0(\tfrac{\boldsymbol{\kappa}}{\nu})$ is the frequency of the phonon mode denoted by wave vector $\boldsymbol{\kappa}$ and dispersion branch ν, and N and n are the total number of unit cells and the number of atoms in the unit cell. The Hamiltonian is the total system energy and is the sum of the mode- and time-dependent kinetic and potential energies, $T(\tfrac{\boldsymbol{\kappa}}{\nu};t)$ and $V(\tfrac{\boldsymbol{\kappa}}{\nu};t)$. The phonon normal mode coordinate, $q(\tfrac{\boldsymbol{\kappa}}{\nu};t)$ and its time derivative, $q(\tfrac{\boldsymbol{\kappa}}{\nu};t)$, are given by

$$
q(\tfrac{\boldsymbol{\kappa}}{\nu};t) = \sum_{\alpha,b,l}^{3,n,N} \sqrt{\frac{m_b}{N}} u_\alpha(\tfrac{l}{b};t)\, e^*(\tfrac{\boldsymbol{\kappa}\ b}{\nu\ \alpha}) \exp[i\boldsymbol{\kappa}\cdot\mathbf{r}_0(\tfrac{l}{0})]
\tag{C2}
$$

and

$$
\dot{q}(\tfrac{\boldsymbol{\kappa}}{\nu};t) = \sum_{\alpha,b,l}^{3,n,N} \sqrt{\frac{m_b}{N}} \dot{u}_\alpha(\tfrac{l}{b};t)\, e^*(\tfrac{\boldsymbol{\kappa}\ b}{\nu\ \alpha}) \exp[i\boldsymbol{\kappa}\cdot\mathbf{r}_0(\tfrac{l}{0})],
\tag{C3}
$$

where m_b is the mass of the bth atom in the unit cell and $\mathbf{r}_0(\tfrac{l}{0})$ is the equilibrium position vector of the lth unit cell. The α-component of the displacement from equilibrium, $u_\alpha(\tfrac{l}{b};t)$,

and velocity, $\dot{u}_\alpha(^l_b; t)$, of the bth atom in the lth unit cell are time-dependent and are related to the phonon mode coordinates through the time-independent eigenvector that has components $e(^{\boldsymbol{\kappa}\ b}_{\nu\ \alpha})$. We start from Eq. (C3) and follow the formulation of anharmonic lattice dynamics theory.[?][?][?][?] In an anharmonic system, the phonon populations fluctuate about the equilibrium distribution function.[?] The phonon mode coordinate for the mode described by $(\boldsymbol{\kappa}, \nu)$ and its time derivative can be written as

$$q(^{\boldsymbol{\kappa}}_{\nu}; t) = q_{SS}(^{\boldsymbol{\kappa}}_{\nu}; t) + q_T(^{\boldsymbol{\kappa}}_{\nu}; t) \tag{C4}$$

and

$$\dot{q}(^{\boldsymbol{\kappa}}_{\nu}; t) = \dot{q}_{SS}(^{\boldsymbol{\kappa}}_{\nu}; t) + \dot{q}_T(^{\boldsymbol{\kappa}}_{\nu}; t) . \tag{C5}$$

The steady-state (SS) and transient (T) parts and their time derivatives are given by

$$\begin{aligned} q_{SS}(^{\boldsymbol{\kappa}}_{\nu}; t) = &C_1(^{\boldsymbol{\kappa}}_{\nu}) \exp[i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) t] \\ &+ C_2(^{\boldsymbol{\kappa}}_{\nu}) \exp[-i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) t], \end{aligned} \tag{C6}$$

$$\begin{aligned} q_T(^{\boldsymbol{\kappa}}_{\nu}; t) = \exp[-\Gamma(^{\boldsymbol{\kappa}}_{\nu}) |t|] \{ &C_3(^{\boldsymbol{\kappa}}_{\nu}) \exp[i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) t] \\ &- C_4(^{\boldsymbol{\kappa}}_{\nu}) \exp[-i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) t] \}, \end{aligned} \tag{C7}$$

$$\dot{q}_{SS}(^{\boldsymbol{\kappa}}_{\nu}; t) = i\omega_0 \left\{ C_1(^{\boldsymbol{\kappa}}_{\nu}) \exp[i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) t] - C_2(^{\boldsymbol{\kappa}}_{\nu}) \exp[-i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) t] \right\} , \tag{C8}$$

and

$$\begin{aligned} \dot{q}_T(^{\boldsymbol{\kappa}}_{\nu}; t) = \exp[-\Gamma(^{\boldsymbol{\kappa}}_{\nu}) |t|] \{ &C_3(^{\boldsymbol{\kappa}}_{\nu}) [i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) - \Gamma(^{\boldsymbol{\kappa}}_{\nu})] \exp[i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) t] \\ &- C_4(^{\boldsymbol{\kappa}}_{\nu}) [i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) + \Gamma(^{\boldsymbol{\kappa}}_{\nu})] \exp[-i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) t] \} , \end{aligned} \tag{C9}$$

where the Cs are constants and $\omega_0(^{\boldsymbol{\kappa}}_{\nu})$ and $\Gamma(^{\boldsymbol{\kappa}}_{\nu})$ are the phonon mode frequency and linewidth. The transient part describes the creation of an excess in the population of a phonon mode for $t < 0$ and its decay back to equilibrium for $t > 0$. Phonon population fluctuations are commonly modeled using the excitation and decay of a single phonon mode (i.e., the single mode relaxation time approximation). In a real system, there will be multiple phonons in each mode that simultaneously grow or decay with time. Thus, dealing only with $\dot{q}$, we let

$$\begin{aligned} \dot{q}(^{\boldsymbol{\kappa}}_{\nu}; t) = \sum_j &i \exp[-\Gamma(^{\boldsymbol{\kappa}}_{\nu}) |t - t_j|] \times \\ &\{ A_j(^{\boldsymbol{\kappa}}_{\nu}) [\omega_0(^{\boldsymbol{\kappa}}_{\nu}) + i\Gamma(^{\boldsymbol{\kappa}}_{\nu})] \exp[i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) (t - t_j)] \\ &- B_j(^{\boldsymbol{\kappa}}_{\nu}) [\omega_0(^{\boldsymbol{\kappa}}_{\nu}) - i\Gamma(^{\boldsymbol{\kappa}}_{\nu})] \exp[-i\omega_0(^{\boldsymbol{\kappa}}_{\nu}) (t - t_j)] \}, \end{aligned} \tag{C10}$$

where many phonons in each mode, indexed by j, are simultaneously being created and destroyed. The phonons grow for $t < t_j$, decay for $t > t_j$, and A_j and B_j are constants. We are not concerned with the values of t_j, A_j, and B_j, though they should satisfy the long-time average $\langle \dot{q}^*(^{\boldsymbol{\kappa}}_{\nu}; t)\, \dot{q}(^{\boldsymbol{\kappa}}_{\nu}; t)\rangle = \langle \dot{q}^*_{SS}(^{\boldsymbol{\kappa}}_{\nu}; t)\, \dot{q}_{SS}(^{\boldsymbol{\kappa}}_{\nu}; t)\rangle$. The expectation value of the kinetic energy of the normal mode in the time domain is

$$\langle T(^{\boldsymbol{\kappa}}_{\nu})\rangle = \frac{1}{2}\lim_{\tau_0 \to \infty}\frac{1}{\tau_0}\int_0^{\tau_0} \dot{q}^*(^{\boldsymbol{\kappa}}_{\nu}; t)\, \dot{q}(^{\boldsymbol{\kappa}}_{\nu}; t)\, dt. \tag{C11}$$

The expectation value of the kinetic energy of the normal mode can be transformed from the time domain to the frequency domain by Parseval's theorem,[?] giving

$$T(^{\boldsymbol{\kappa}}_{\nu}; \omega) = \lim_{\tau_0 \to \infty}\frac{1}{2\tau_0}\left|\frac{1}{\sqrt{2\pi}}\int_0^{\tau_0} \dot{q}(^{\boldsymbol{\kappa}}_{\nu}; t)\exp(-i\omega t)dt\right|^2. \tag{C12}$$

By substituting Eq. (C10) into Eq. (C12) and performing the time integration we find

$$T(^{\boldsymbol{\kappa}}_{\nu}; \omega) = \frac{1}{16\pi\tau_0}\left|\sum_j \exp[-i\omega t_j]\left\{A_j(^{\boldsymbol{\kappa}}_{\nu})\frac{\omega_0(^{\boldsymbol{\kappa}}_{\nu}) + i\Gamma(^{\boldsymbol{\kappa}}_{\nu})}{\omega_0(^{\boldsymbol{\kappa}}_{\nu}) - \omega + i\Gamma(^{\boldsymbol{\kappa}}_{\nu})}\right.\right.$$
$$\left.\left. + B_j(^{\boldsymbol{\kappa}}_{\nu})\frac{\omega_0(^{\boldsymbol{\kappa}}_{\nu}) - i\Gamma(^{\boldsymbol{\kappa}}_{\nu})}{\omega_0(^{\boldsymbol{\kappa}}_{\nu}) + \omega - i\Gamma(^{\boldsymbol{\kappa}}_{\nu})}\right\}\right|^2. \tag{C13}$$

We are primarily interested in values of ω where $\omega \approx \omega_0$ when $\Gamma << \omega_0$ (this condition is met for the three systems studied here). When $\omega \approx \omega_0$, the term involving A_j becomes large and the term involving B_j can be neglected (alternatively, we could ignore the term involving A_j when $\omega \approx -\omega_0$). Hence, we find

$$T(^{\boldsymbol{\kappa}}_{\nu}; \omega) = \frac{1}{16\pi\tau_0}\sum_j\sum_{j'}\cos\left[\omega(t_{j'} - t_j)\right]A_j(^{\boldsymbol{\kappa}}_{\nu})\,A_{j'}(^{\boldsymbol{\kappa}}_{\nu})$$
$$\times \frac{\omega_0^2(^{\boldsymbol{\kappa}}_{\nu}) + \Gamma^2(^{\boldsymbol{\kappa}}_{\nu})}{\Gamma(^{\boldsymbol{\kappa}}_{\nu})}\frac{\Gamma(^{\boldsymbol{\kappa}}_{\nu})}{[\omega_0(^{\boldsymbol{\kappa}}_{\nu}) - \omega]^2 + \Gamma^2(^{\boldsymbol{\kappa}}_{\nu})}. \tag{C14}$$

We arrive at the expression for the phonon spectral energy density for the wavevector $\boldsymbol{\kappa}$ by summing Eq. (C14) over the different polarizations ν,

$$\Phi(\boldsymbol{\kappa}, \omega) = 2\sum_\nu^{3n} T(^{\boldsymbol{\kappa}}_{\nu}; \omega) = \sum_\nu^{3n} C_0(^{\boldsymbol{\kappa}}_{\nu})\frac{\Gamma(^{\boldsymbol{\kappa}}_{\nu})/\pi}{[\omega_0(^{\boldsymbol{\kappa}}_{\nu}) - \omega]^2 + \Gamma^2(^{\boldsymbol{\kappa}}_{\nu})}, \tag{C15}$$

where the factor of two comes from equipartition of kinetic and potential energy (valid for a harmonic classical system), and

$$C_0(^{\boldsymbol{\kappa}}_{\nu}) = \sum_j\sum_{j'}\cos\left[\omega(t_{j'} - t_j)\right]A_j(^{\boldsymbol{\kappa}}_{\nu})\,A_{j'}(^{\boldsymbol{\kappa}}_{\nu})\frac{\omega_0^2(^{\boldsymbol{\kappa}}_{\nu}) + \Gamma^2(^{\boldsymbol{\kappa}}_{\nu})}{8\tau_0\Gamma(^{\boldsymbol{\kappa}}_{\nu})}. \tag{C16}$$

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Thus, the phonon spectral energy density $\Phi(\boldsymbol{\kappa}, \omega)$ is a superposition of $3n$ Lorentzian functions with centers at $\omega_0(^{\boldsymbol{\kappa}}_{\nu})$ (one for each polarization) with a linewidth (half-width at half-maximum) of $\Gamma(^{\boldsymbol{\kappa}}_{\nu})$. Φ is a spectral energy density since its integral over all wavevectors and frequencies is the total crystal energy, i.e., the Hamiltonian is

$$H = \int_{V_{BZ}} \int_0^\infty \Phi(\boldsymbol{\kappa}, \omega) d\omega d\boldsymbol{\kappa}, \tag{C17}$$

where V_{BZ} is the volume of the first Brillouin zone. Like the frequency broadening, there is also a broadening of the SED in wavevector.[?] For a finite sampling of the first Brillouin zone, the Hamiltonian can be approximated by

$$H \approx 2 \sum_{\boldsymbol{\kappa}, \nu}^{N, 3n} \langle T(^{\boldsymbol{\kappa}}_{\nu}; t) \rangle = \sum_{\boldsymbol{\kappa}}^N \int_0^\infty \Phi(\omega, \boldsymbol{\kappa}) d\omega. \tag{C18}$$

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[1] Y. He, D. Donadio, and G. Galli, Applied Physics Letters **98**, 144101 (2011).

[2] J. E. Turney, E. S. Landry, A. J. H. McGaughey, and C. H. Amon, Physical Review B **79**, 064301 (2009).