

Predicting Vibrational Mean Free Paths in Amorphous Materials

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Understanding thermal transport in crystalline systems requires detailed knowledge of phonons, which are the quanta of energy associated with atomic vibrations. By definition, phonons are non-localized vibrations that transport energy over distances much larger than the atomic spacing. For disordered materials (e.g., alloys, amorphous phases), with the exception of very long wavelength modes, the vibrational modes are localized and do not propagate like phonons. The Einstein model assumes that the mean free path of these localized vibrations is the average interatomic distance and that their group velocity is equal to the speed of sound. The Cahill-Pohl model assumes that the mean free path of the localized modes is equal to half of their wavelength. While these approach can be used to estimate the thermal conductivity of disordered systems, they only provide a qualitative description of the vibrations that contribute to the lattice thermal conductivity. Using lattice dynamics calculations and molecular dynamics simulations on model amorphous silicon and silica, we predict and characterize the contributions from phonons and localized vibrations to lattice thermal conductivity. The vibrational mean free paths are predicted for these two amorphous materials and the thermal conductivity accumulation function is compared with recent experimental results.

I. INTRODUCTION

The thermal conductivity of amorphous solids display unique temperature dependance compared to ordered solids.[?] Cahill argued that the lattice vibrations in a disordered crystal are essentially the same as those of an amorphous solid.[?]

Measurements by all the refs from Galli paper, including Moon.^{???} 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. Thermal transport will be studied to quantify and characterize the ordered and disordered contributions to lattice thermal conductivity. In particular, a more rigorous way to classify vibrational modes in disordered alloys and amorphous samples as phonon-like or diffuson will be investigated. These results will be compared to the phenomenological Einstein and Cahill-Pohl models.^{???}

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

II. THERMAL CONDUCTIVITY THEORY AND FORMULATION

A. Phonon Theory

$k = \text{sum over modes}$

For a perfect system, all vibrational modes are phonons.

$$k_{vib,n} = \sum_{\kappa} \sum_{\nu} c_{ph}(\kappa) v_{g,n}^2(\nu) \tau(\kappa). \quad (1)$$

Of particular interest is the phonon mean free path (MFP),

$$\Lambda(\kappa) = |v_g| \tau(\kappa), \quad (2)$$

which requires a group velocity.

1. Phonon Diffusivity

Taking the phonon mode specific heat to be $c_{ph}(\nu) = k_B$, the phonon mode specific vibrational conductivity

(Eq. (??)) can be written as

$$k_{vib,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} k_B D_{ph}(\kappa_{\nu}), \quad (3)$$

and the vibrational conductivity is determined by the phonon mode diffusivities, defined as

$$D_{ph}(\kappa_{\nu}) = v(\kappa_{\nu})^2 \tau(\kappa_{\nu}). \quad (4)$$

This concept is useful for understanding how the relevant phonon properties (lifetime and group velocity) affect the thermal transport. It is also useful for comparing the relative transport strength of diffusons and phonons. Fig. 8 plots the phonon and diffuson mode diffusivities of a 256 atom LJ crystal and amorphous system at $T = 20$ K. The number of vibrational modes is the same for these two systems, but the relative magnitudes of the diffusivities vary greatly. The phonons diffusivities are generally greater than the diffuson diffusivities. However, Brillouin zone boundary (see Section ??) phonon modes have a finite lifetime but vanishing group velocities, giving $D_{ph}(\kappa_{\nu}) = 0$.[?] For crystalline systems with many atoms in the unit cell, the presence of optical phonon modes begins to trap heat in low-group velocity branches ($D_{ph}(\kappa_{\nu}) \approx 0$, see Section ??), making the distinction between phonons and diffusons difficult. Based on their contribution to vibrational conductivity, these low diffusivity optical phonons are thermally indistinguishable from diffusons. The parameters defining the phonon diffusivity (phonon lifetime and group velocity) are generally well-understood. In particular, design strategies to minimize both of these parameters exist (see Sections ?? and ??). However, the design strategies to control the diffusons diffusivities (D_{AF}) are not well understood.^{??} The diffuson theory does not consider the effects of anharmonicity, which can be investigated using a combination of MD simulations and LD calculations.[?]

B. Diffuson Theory

The models for phonon scattering mechanisms described in Section ?? are successful for dilute alloys ($c < 0.1$).^{??} However, as the alloy concentration is increased, the vibrational modes become localized and non-propagating and a new description of the vibrational modes which carry the heat is required.

For even more disordered systems, such as amorphous materials, the thermal transport is modeled using completely localized vibrations (called *diffusons*) which propagate diffusively, as phonons do.[?] However, the propagation of these diffusons is (typically) much slower than the propagation of phonons which are able to carry heat over long distances before scattering. Thus, the vibrational conductivity of amorphous phase is typically several orders of magnitude less than crystalline phase.^{??}

The diffuson theory of Allen and Feldman is different than the phenomenological models discussed in Section ?? in that the only allowed wavevector is strictly $\kappa = 0$ since the system is disordered. In reality, the vibrational conductivity has contributions from very-long wavelength phonon-like modes (see Section ??).

The disordered contribution to vibrational conductivity, k_{AF} , is given by

$$k_{AF} = \sum_i C(\omega_i) D_{AF}(\omega_i) \quad (5)$$

where $C(\omega_i)$ and $D_{AF}(\omega_i)$ are the diffuson mode specific heat and diffusivity.

The vibrational conductivity at low temperatures in disordered and amorphous materials is due to the low temperature behavior of the specific heat $C(\omega_i)$, which is dictated by Bose-Einstein statistics.[?] The theory of Allen and Feldman is purely harmonic. In the classical harmonic limit, $C(\omega_i) = k_B$ and k_{AF} is temperature independent, which can be used to understand the amorphous LJ temperature independence of vibrational conductivity in Section ??.

Diffusons, locons and propagons[?].

C. Vibrational Thermal Diffusivity

Allen Feldman theory[?].

Feldman measure the DOS using the average level spacing.[?]

Predictions for a-Si, also effects of mass disorder.[?] : is Di pinned near a value of Di (1/3)va?

$$D = 1/3 v_s a$$

It was noticed by Birch and Clark (1940), and by Kittel (1948) that in glasses (T) at $T \approx 20$ K could be interpreted as the specific heat $C(T)/V$ multiplied by a temperature-independent diffusivity D of order $a^2 D/3$ where a is an interatomic distance. In the phonon-gas model, this would correspond to $1/a$, too small to justify 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 $1/a$, 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 certainly lies low in the spectrum of a glass) should lie close to the E/L boundary.

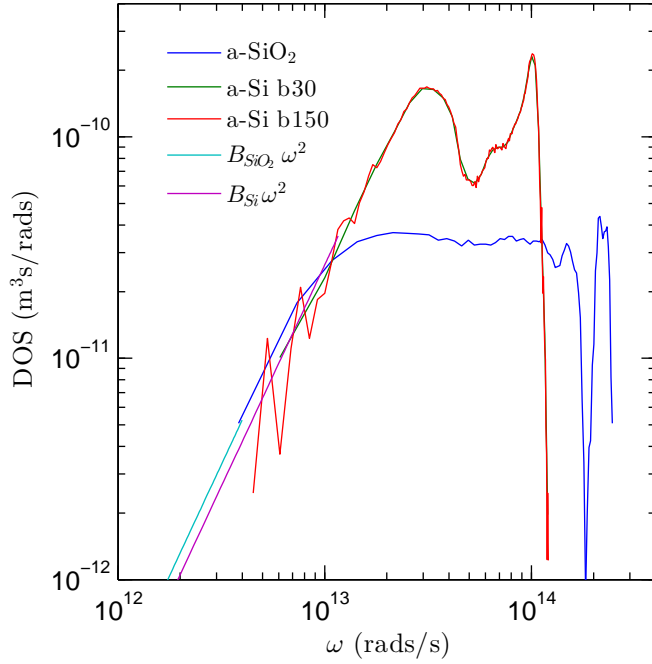


FIG. 1: film thickness dependant thermal conductivity of a-Si from experiment.

III. SIMULATION DETAILS

IV. SAMPLE PREPARATION

We use models created by the WWW algorithm as described in⁷.

Alternatively, amorphous samples are made by a melt-quench procedure. The crystal phase is melted at a high temperature (20,000 K for silicon) at constant volume. The liquid is then quenched to a temperature

structural relaxation: a-LJ, a-sio2,a-Si. Both a-sio2 and a-Si require annealing at high temperature (about 1/2 Tmelt) to allow structural relaxation.

structural relaxation: U1 = 7.64X10 m/s and UT = 3.67X10, indicates that there has been structural relaxation vs_long : 8.2715e + 03, vs_t ran : 3.8867e + 03

V. DENSITY OF STATES

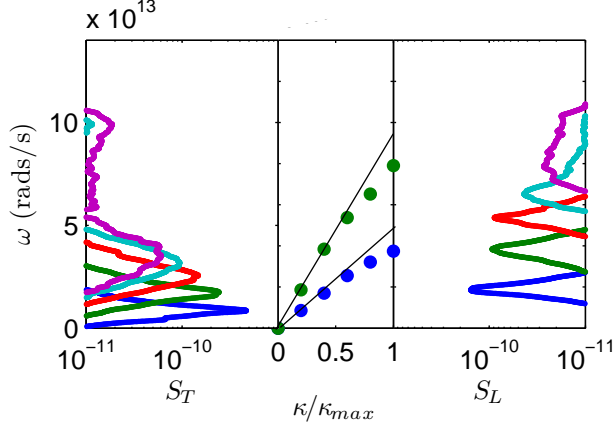


FIG. 2: film thickness dependant thermal conductivity of a-Si from experiment.

VI. GROUP VELOCITY FROM STRUCTURE FACTOR

Fig 4 of this work shows a dispersion extracted by locating the peaks in the structure factor.[?]

Fig. 5 discusses how since the low freq modes are sparse, there is a resonant effect between[?]

If all modes are summed over, this gives the frequency spectrum needed to construct a (nonstationary) propagating state with a pure wave vector \mathbf{Q} and pure longitudinal or transverse polarization[?]. Locations of spectral peaks are peaked like a acoustic dispersion branches. Only low-frequency vibrations have an (approximate) wavevector in disordered systems, and there is no theorem guranteeing this.[?]

However, it is very difficult to distinguish between localized and extended modes at high frequencies on the basis of their $S(k, \nu)$ functions, as illustrated by the very similar scattering functions for a 67-meV localized and a 63-meV extended mode in Fig. 3(b).[?]

The dynamic structure factor can be useful for demonstrating the plane-wave character of low-frequency vibrations. However, on a mode-by-mode basis, it is unable in general to characterize a given mode as either localized or delocalized. Thus, it is not possible to

The structure factor at a VC wave vector $\mathbf{\kappa}_{VC}$ is defined as[?]

$$S^{L,T} = \sum_{\nu} E^{L,T} \delta[\omega - \omega_{\nu}], \quad (6)$$

where the summation is over the Gamma modes, E^T refers to the transverse polarization and is defined as

$$E^L = \left| \sum_b \hat{\mathbf{\kappa}}_{VC} \cdot \mathbf{e} \exp[i\mathbf{\kappa}_{VC} \cdot \mathbf{r}_0^{(l=0)}] \right|^2 \quad (7)$$

and E^L refers to the longitudinal polarization and is de-

fined as

$$E^T = \left| \sum_b \hat{\mathbf{\kappa}}_{VC} \times \mathbf{e} \exp[i\mathbf{\kappa}_{VC} \cdot \mathbf{r}_0^{(l=0)}] \right|^2. \quad (8)$$

In Eqs. (7) and (8), the b summations are over the atoms in the disordered supercell, $\mathbf{r}_0^{(l=0)}$ refers to the equilibrium atomic position of atom b in the supercell, l labels the unit cells ($l = 0$ for the supercell), α labels the Cartesian coordinates, and $\hat{\mathbf{\kappa}}_{VC}$ is a unit vector. Explicit disorder is included in the Gamma frequencies ω and the $3N_a$ components of the eigenvectors, \mathbf{e} .

$$(\mathbf{\kappa}, \omega) = \frac{1}{N\tau_0} \left| \sum_b^N \sum_{\alpha^3} \int_0^{\tau_0} u_{\alpha} \exp[\Theta] dt \right|^2, \quad (9)$$

where $\Theta \equiv i[\mathbf{\kappa} \cdot \mathbf{r}_0^{(l)} - \omega t]$.

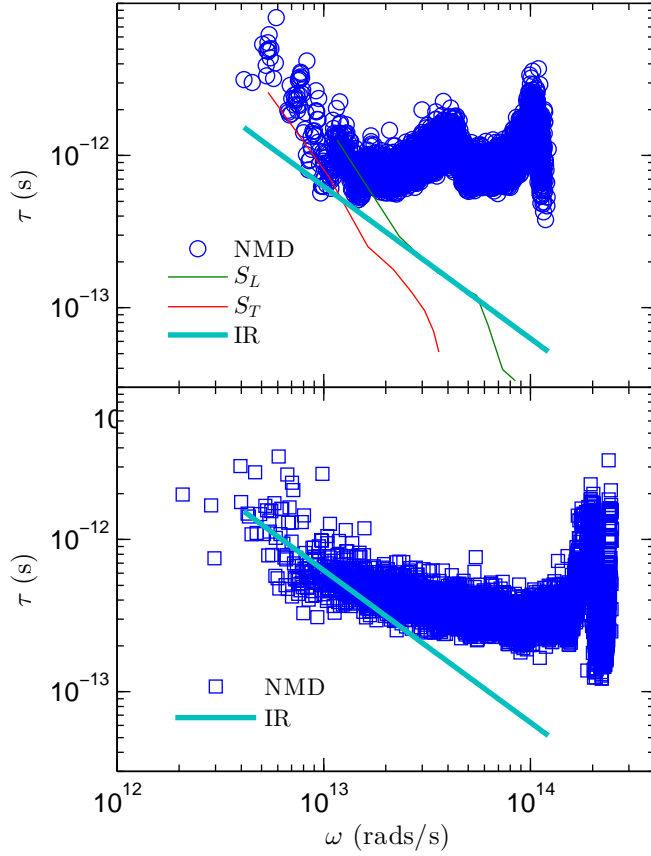


FIG. 3: film thickness dependant thermal conductivity of a-Si from experiment.

VII. LIFETIMES

Lifetimes in amorphous silicon predicted before using a normal mode approach, but mode-by-mode properties were not presented.[?]

Lifetimes were predicted using anharmonic lattice dynamics, but no thermal transport properties were predicted.[?]

Thermal diffusivity was predicted for a percolation network which showed Rayleigh type scattering dependence in the low-frequency limit.[?]

Thermal diffusivity has been predicted using a wave-packet method

The lifetimes of vibrational modes in a-Si were predicted using normal mode decomposition.[?]

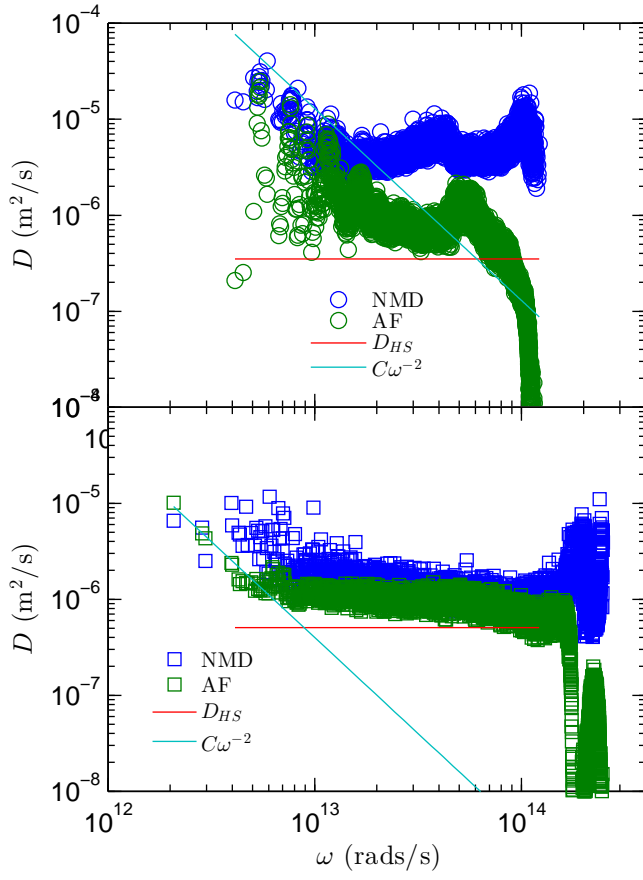


FIG. 4: film thickness dependant thermal conductivity of a-Si from experiment.

VIII. AF DIFFUSIVITIES

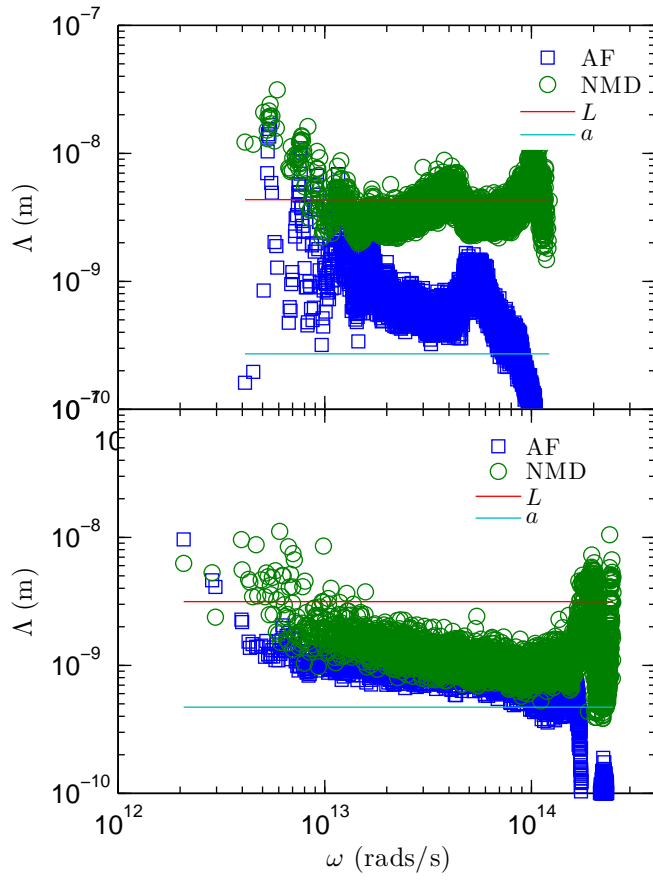


FIG. 5: film thickness dependant thermal conductivity of a-Si from experiment.

IX. MEAN FREE PATHS

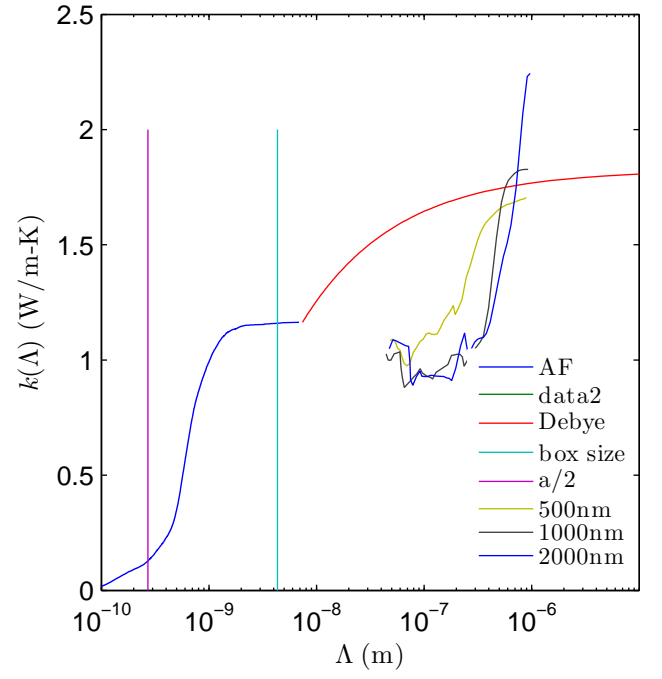
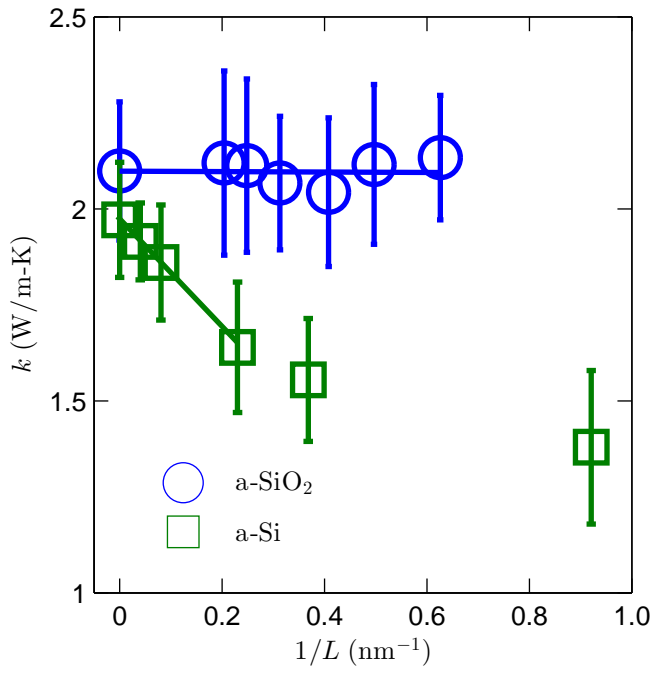


FIG. 7: film thickness dependant thermal conductivity of a-Si from experiment.

X. THERMAL CONDUCTIVITY

$$k = \int_0^{\omega_{max}} \frac{d\omega DOS(\omega) C(\omega/T) D(\omega)}{V} \quad (10)$$

$$C(\omega/T) = k_B \frac{\hbar\omega/2k_BT}{\sinh(\hbar\omega/2k_BT)}^2 \quad (11)$$

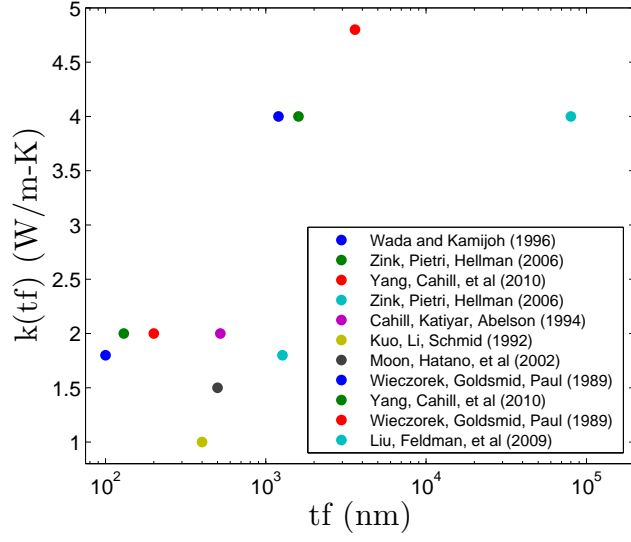


FIG. 8: film thickness dependant thermal conductivity of a-Si from experiment.

XI. EXPERIMENTAL RESULTS

APPENDIX A: PREDICTING VIBRATIONAL LIFETIMES

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