Evaluation of the Virtual Crystal Approximation for Predicting Thermal Conductivity

Alloy Phonon Properties and

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only one

— specifically state what will be compared and to what

Abstract

In this work, the virtual crystal approximation for mass disorder is evaluated by examining two model alloy systems: Lennard-Jones argon and Stillinger-Weber silicon. In both cases the perfect crystal is alloyed with a heavier mass species up to equal concentration and phonon properties *be more specific* and thermal conductivity are predicted. These two alloy systems have different ranges of phonon frequencies, lifetimes, and mean free paths. For Stillinger-Weber silicon, the virtual crystal approximation predicts phonon properties and thermal conductivity in good agreement with molecular dynamics-based methods. For Lennard-Jones argon, the virtual crystal approximation underpredicts the high-frequency phonon lifetimes, leading to an underpredicting of its thermal conductivity. Resolution of these underpredictions is achieved by considering methods that treat the disorder explicitly.

both needed?

— lots of references to upcoming sections needed?

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I. INTRODUCTION

③ Predicting the thermal conductivity of disordered ~~lattices~~ /materials/ ~~dates back to...~~ In the case of dielectrics semiconductors, almost all of the heat is conducted by the vibrational modes of the system. Understanding the mechanisms that lead to the scattering of these ~~vibrations~~ transport (3) of these vibrational modes is crucial for predicting ~~the~~ thermal conductivity ~~of disordered lattices~~.

there are other important applications — solar cells, thermal barrier coatings, transport properties.

⑦ To improve the efficiency of thermoelectric devices, ~~efforts to reduce thermal conductivity using several techniques, including micro- and nano-boundary scattering. These techniques often require complicated nanostructuring and manufacturing techniques.~~ Alloying remains an effective method to reduce ~~the~~ thermal conductivity while maintaining good electrical ~~of materials.~~ In particular, for materials with short phonon mean free path ~~spectra~~, alloying is ~~still~~ a potential thermal conductivity reduction mechanism where nanostructuring is not.[1]

④ Accurately predicting the thermal conductivity of a dielectric or semiconducting material requires the properties of phonons from the entire Brillouin zone. too specific here? Accurate predictions of ~~these~~ ~~phonon~~ properties for bulk systems, where the vibrational modes are phonon modes, can be made with anharmonic lattice dynamics (ALD) theory using ab initio calculations.[1-7] tells However, computational costs limit the size of computational cells in ab initio calculations to be less than 100 atoms, making it difficult to explicitly directly incorporate the effects of disorder.[1,3,4,9]

Recently work using ab-initio calculations, anharmonic lattice dynamics (ALD), and the virtual crystal (VC) approximation ~~was done to~~ ed predict phonon mode frequencies, lifetimes and group velocities of ~~defected materials~~ alloys with ~~realtively~~ large[3,4] and small[1] thermal conductivities quantities. Under ~~this~~ etc approximation, the disordered ~~crystal~~ solid is replaced with a perfect virtual crystal with properties equivalent to an averaging over the disorder (e.g. mass or bond strength).[10] The use of ALD with the VC approximation (referred to herein as VC-ALD) can thus base all calculations on a small unit cell with averaged properties and treats the effects of intrinsic and disorder scattering as perturbations ~~rather than including disorder explicitly.~~[1,3,10,11] ~~However,~~ No comprehensive study has been performed to assess the applicability of this perturbative approach for a range of disorder meaning what? using multiple predictive methods and test systems.

The goal of this work is to investigate the use of the VC approximation for predicting thermal conductivity of disordered lattices by a detailed comparison of three predictive methods: vibrational mode properties and active (i) (ii) MD based normal mode decomposition (NMD, Section), and Green-Kubo (GK, Section ??), MD-based and VC-ALD ~~which treats the harmonic and anharmonic phonon scattering as perturbations~~

② by "disordered lattice" do you mean "alloy"?

~~(Section II.2)~~. Two model binary-alloy systems (labeled as $m_{1-c}^a m_c^b$, Section) with varying concentrations (c) of mass defects are considered: Lennard-Jones (LJ) argon and Stillinger-Weber (SW) silicon. In both cases the perfect crystal is alloyed with a heavier mass species up to equal concentration ($c = 0.5$), spanning a range of perturbative to heavy disorder. By spanning this range, the limits of the perturbative models are examined. *Good*

The LJ argon and SW silicon alloyed systems have ~~very~~ different ranges of phonon frequencies, lifetimes, group velocities and total thermal conductivity. For SW silicon, VC-ALD predicts thermal conductivity in good agreement with the explicitly disordered method GK (Section). For LJ argon, VC-ALD underpredicts the high frequency phonon lifetimes, leading to an underpredicting of ~~the~~ thermal conductivity when compared to the explicitly disordered methods VC-NMD and GK (Section). The different thermal conductivity spectra and the breakdown of the perturbative models are examined. Resolution of the breakdown is achieved by including the explicit effect of disorder on the thermal transport of vibrational modes (Section). Based on the effects of explicit disorder, a simple guideline is suggested for use with the VC approximation.

not used yet... Experimental measurements of isotopically pure and Ge-doped Si epitaxial layers demonstrate the original theory by Abeles can predict thermal conductivity in dilute alloys. Abeles also found good agreement with dilute predictions for both experimental measurements of both Si-Ge alloys and also (Ga,In)As alloys.[10] However, both of these alloy systems have a relatively high thermal conductivities (on the order of 1-10 W/m-K at 300 K). However, in the heavily disordered system In(As,P) (mass ratio of 3.7) worse agreement with the Abeles theory is observed.

II. Theoretical and Modeling Formulation

A. Virtual Crystal ~~(VC)~~ Approximation

Abeles first introduced the idea of using a ~~virtual crystal (VC)~~ to replace a disordered system, computing the thermal conductivity of Si/Ge alloys by treating ~~both~~ disorder and anharmonicity as perturbations.[10] Many experimental trends in thermal conductivity of a range of materials can be explained using the VC approximation.(cite) For example, the reduced thermal conductivity of Ge versus Si is partly explained by both the increased mass and decreased bulk modulus (stiffness) of the lattice,(cite) which has the effect of reducing the phonon group velocities. The same effect can be seen in alloy systems.(cite) Sound

-mention diffusivity?

this paragraph isn't great maybe easier once more of paper is complete

-refer to Abeles in (3) above with a brief comment on theory integrate

need section heading

What is the point of this section?

needed? a bit confusing to discuss perfect crystals in this context

more detail, fittings?

Comment on agreement with experiment

speeds of alloys: CRC, (Cahill-Pohl).

A complete description of the thermal transpot in ~~both~~ perfect crystals and alloys requires modeling ~~the~~ intrinsic and disordered scattering to calculate phonon lifetimes (see Section IF 2). Phonon lifetimes can be predicted ~~by treating both the intrinsic and disorder scattering~~ using perturbation theory (Section). While the theory ~~which~~ that treats phonon defect scattering ~~(Eq.)~~ is valid for perturbative disorder, its use leads to good agreement with ~~several~~ experimental and computational results, with large disorder. Cahill ~~shows~~ that conductivty reduction in dilute Ge-doped Si epitaxial layers ~~is captured~~ by mass perturbative disorder.[12,13] While the mass disorder was large ($m_{Ge}/m_{Si} = 2.6$), the overall disorder strength is dictated by the concentration. As little as $6.2 \times 10^{19} cm^{-3}$ Ge ($g_2 = 3.1 \times 10^{-3}$, see Section) is enough to reduce the thermal conductivity ~~of Si~~ by almost a factor of 2.[12] Even in the case of $Ni_{0.55}Pd_{0.45}$, with large mass disorder and concentration ($m_{Pd}/m_{Ni} \approx 2$, $g_2 = 0.078$ Section), good agreement is also seen using a VC approach.[14] What is thermal conductivity of NiPd alloy versus amorphous phase, what is the HS prediction.

Computational ~~results~~ using the VC approximation for high thermal conductivity alloys show good to excellent agreement with experimental results.[3,4] Garg used ab initio calculations with VC-ALD to predict the thermal conductivity of Si/Ge alloys ~~for all concentrations~~, obtaining excellent agreement with experiment.[4] Does Garg find factor of 2 change for intrinsic lifetimes, or the combination of intrinsic and defect with Matthiesen rule? Lindsay and Broido found good agreement ~~with~~ VC-ALD and experiment for isotopically defected GaN.[3] Isotopically defected GaN and Si/Ge alloys ~~(even for large concentrations c, Section)~~ have relatively large thermal conductivities.(cite) In particular, the conductivity of Si/Ge alloys is significantly larger than that of the high scatter limit ~~(Section)~~. A detailed study of low thermal conductivity materials PbTe[5] and PbTe/PbSe[1] made predictions for the perfect systems in fair agreement with experiment, where results lack for the alloys. What is the PbTe HS prediction. Thus, there is a need to examine the perturbative approach of VC-ALD for heavily disordered systems. The computational studies discussed above were limited to the use of VC-ALD because of the computational cost of ab initio calcualtions. Computationally cheap empirical potentials can be used to incude the effects of disorder explicitly.

Using computationally-cheap empirical potentials for argon and silicon[15], we study the effects of disorder explicitly. Using the VC approximation, we perform calculations at dif-

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ferent concentrations (c) of mass varying ($m_{1-c}^a m_c^b$) binary alloys of Lennard-Jones argon and Stillinger-Weber silicon (Section). We predict the phonon mode properties of the VC: frequencies (Section), group velocities (Section), and lifetimes (Section), and use them to predict thermal conductivity (Section). Methods referred to as VC-NMD (Section) and VC-ALD (Section) use the VC approximation. Explicit disorder is examined using lattice dynamics (LD) calculations (Section and), Allen-Feldman theory (Section),[16] and molecular dynamics (MD) simulations (Section). The breakdown of the perturbative VC-ALD method is examined (Section), and a simple correction is suggested by predictions from the AF theory (Section).

dunno where this belongs

While the group velocities are necessary to predict ~~the~~ thermal conductivity, of particular interest is the phonon mean free path (MFP),

$$\Lambda\left(^\kappa_\nu\right) = |v_g|\tau\left(^\kappa_\nu\right),$$ (1)

which is crucial for understanding nano and micro-nanostructuring effects.(cite) It is correct to regard the mode lifetime $\tau\left(^\kappa_\nu\right)$ as the more fundamental quantity is a disordered system,(cite) since there is no general way to predict the group velocities of disordered modes.(cite) The effect of disorder on mode group velocities is examined in (Section) and (Section).

B. Thermal Conductivity ~~Models~~ Prediction

To predict the thermal conducitivty of disordered lattices, one begins with the theory for a perfect lattice. For a perfect lattice, all vibrational modes are phonons, which by defintion are delocalized, propagating plane waves.(cite) Using the single-mode relaxation time approximation[18] ~~as an approximate solution of~~ to solve the Boltzmann transport equation[19] gives an expression for thermal conductivity,

$$k_{ph,\mathbf{n}} = \sum_\kappa \sum_\nu c_{ph}\left(^\kappa_\nu\right) v_{g,\mathbf{n}}^2\left(^\kappa_\nu\right) \tau\left(^\kappa_\nu\right).$$ (2)

Here, the phonon mode has frequency $\omega\left(^\kappa_\nu\right)$ ~~(Section)~~, c_{ph} is the phonon volumetric specific heat, $v_{g,\mathbf{n}}$ is the component of the group velocity vector in direction $\mathbf{n}$ ~~(Section)~~, and $\tau\left(^\kappa_\nu\right)$ is the phonon lifetime ~~(Section)~~. The SMRT approximation has been shown to be accurate for

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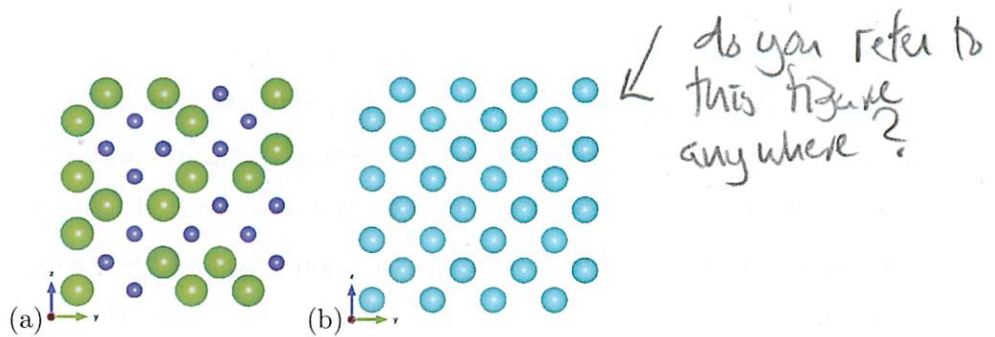*[handwritten: do you refer to this figure anywhere?]*

FIG. 1: (a) view of an explicitly disordered supercell of Si and "heavy" Si ([100] direction into the paper).[17] (b) view of the equivalent VC supercell with an average mass of the explicitly disordered Si and "heavy" Si supercell (b). Sphere size represents increasing mass only, no bond disorder is considered. In this work, calculations for LJ Ar and SW Si which use the VC approximation are based off of the conventional cubic unit cells (Section I D, ??, I F 1 and I F 2). The explicitly disordered supercells are used in Sections I D, I E 2, I F 1 and ??.

[handwritten: alloy or crystal?]

Si/Ge systems and lower thermal conductivity materials, while larger conductivity materials such as GaN and Diamond require a full iterative solution to the BTE for more accureate *[handwritten: predictions]* results.[2]

For the perfect cubic lattices considered in this work (see Section), the lattices and the components of their thermal conductivity are cubically symmetric, so that we refer to k_{ph} *[handwritten: as a scalar]* only. This is also true for the disordered lattices in the long wavelength limit. Since the MD simiulations we perform (Section)are classical and obey Maxwell-Boltzmann statistics,[20] the specific heat is k_B/V per mode in the harmonic limit, where V is the system volume. This approximation has been shown to be valid for LJ Ar(cite SED or ASME?) and SW Si(cite SED or ASME?) and is used for all calculations in this work so that direct comparisons can be made for all methods.

[handwritten: Therm. cond. symmetry exists; needed?; between]

In the classical-harmonic limit, the thermal conductivity is determined by the thermal diffusivity of each mode, which for phonons is the product of the group velocity and lifetime (see Section). For the perturbative VC-ALD models (Section), the group velocities are calculated from the dispersion curves and the lifetimes computed by Eq without the use of explicit disorder. For VC-NMD, the group velocities are calculated from the dispersion curves and the lifetimes predicted from MD simulation with explicit disorder (Section).

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For explicitly disordered systems, the Allen-Feldman (AF) theory computes the contri-

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bution of diffuson modes to vibrational conductivity (Section) and was developed to predict the thermal conductivity of a-Si.[16] In the AF theory, the thermal conductivity is written as

$$k_{AF} = \sum \frac{k_B}{V} D_{AF}(\omega(\nu)),$$ (3)

where D_{AF} is the mode-specific thermal diffusivity of disordered vibrational modes defined at the wavevector [000] (referred to as Gamma, Section). The relative contribution of both phonons and diffusons to the total vibrational conductivity, $k_{vib} = k_{ph} + k_{AF}$, has been estimated for a-Si.[21] While studies have been performed on alloying the amorphous phase, the AF theory has not been applied to disordered lattices.[22] In the current study of disordered lattices, the AF theory predictions help to provide a lower limit for the contribution of a given vibrational mode to thermal transport within the computational framework of the VC approximation (Section). This is essential given the computational cost of the AF theory (Appendix), and is also convienient given the simplicity of the VC computational framework.

C. Simulation Details

Perfect and explicitly disordered lattice supercells are generated with atomic positions based on LJ argon's FCC ($n = 4$) and silicon's diamond-FCC ($n = 8$) crystal structure, where n is the number of atoms in the unit cell. Supercells are built cubically with size N_0, where N_0 refers to the number of repetitions of the unit cell in all 3 spatial directions. Supercells up to size N_0 12 for LJ argon (6096 atoms) are used for calculations. For SW silicon, $N_0 \leq 10$ (SW silicon, 8000 atoms) are used for the MD-based methods, and $N_0 \leq 38$ for VC-ALD (see Appendix D).

Disorder is created by randomly specifying the masses of the atoms on the lattice. The composition of the lattices is labeled by $m^a_{1-c} m^b_c$, where $m^a = 1$ and $m^b = 3$ in LJ units for argon and $m^a = m_{Si}$ and $m^b = 2.6 m_{Si}$ for SW silicon and "heavy silicon" (mass of germanium). For c = 0.5, the LJ VC has average mass of 2. The supercells are built using the zero-pressure finite-temperature lattice constants for LJ argon, which are $a = 1.556$ (T=10 K) and and $a = 1.580$ (T=40 K) in LJ units.[23] For LJ argon, the variation of lattice constant with composition is small and ignored. The effective zero-pressure lattice constant of the amorphous phase at T=10K is slightly larger ($a = 1.585$).[23] All LJ calculations

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use these lattice constants. For SW silicon, the lattice constant $a = 5.43\AA$ is used for all

calculations, which brings the GK thermal conductivty predictions[24] into better agreement

with VC-ALD[25] for $c = 0.0$ (Section).

III Vibrational Mode Properties in Alloy Systems

D. VC and Gamma DOS

In this section, we examine the effect of explicit disorder by computing the density of

states (DOS, $D(\omega(_\nu^\kappa))$) for vibrational modes of and of the disordered lattice supercells and

their equivalent VCs. Each vibrational mode contributing to the thermal conductivity has

a frequency $\omega(_\nu^\kappa)$. The allowed frequencies are the sqaure root of the eigenvalues of the

system's Dynamical matrix, $D(\kappa)$,[26] which relates the normal mode eigenvector ($e(_\nu^\kappa)$) and

eigenvalue by

$$D(\kappa)e(_\nu^\kappa) = \omega^2(_\nu^\kappa)\,e(_\nu^\kappa).\tag{4}$$

The set of eigenvalues and eigenvectors are the othonormal basis of the vibrational lattice.[26]

In a perfect system all vibrational (normal) modes are plane-waves, and as such can be

identified by a wave-vector κ, eigenvector $e(_\nu^\kappa \,_\alpha^b)$, and a possibly degenerate frequency $\omega(_\nu^\kappa)$.

Here, b labels the atom in the unit cell, α labels the cartesian coordiantes, and ν labels

the mode polarization (possibly degenerate in frequency). In a disordered system, such as

a lattice supercell with randomly arranged and differing mass species, all normal modes

exist at the wavevector [000], where $n = N_a$ and $\nu \leq 3N_a$, where N_a is the total number

of atoms in the system. However, for small disorder ($c \approx 0$), the modes of the disordered

lattice are nearly plane-waves. In general, normal modes in a disordered system will not

be pure plane-waves and will be non-degenerate in frequency. We compare the ordered and

disordered normal mode frequencies in Section ?? and mode eigenvectors in Section for the

full range of disorder ($c \leq 0.5$).

With the appropriate dynamical matrix ($\kappa = [000]$ for the explicitly disordered lattice

supercells), the frequencies are computed using the program GULP.[27] For the VC, the fre-

quencies are identified (up to polarization) by the list of wavevectors allowed by the size

of the lattice supercell. (cite) The DOS for the VC and the explicitly disordered supercells

(referred to herein as Gamma) are shown in Fig. The VC and Gamma agree at low fre-

quencies, where the Debye approximation predicts $DOS \propto \omega^2$.(cite) The Debye approx-

imation underpredicts the the DOS at moderate frequency, which is due to the non-linear

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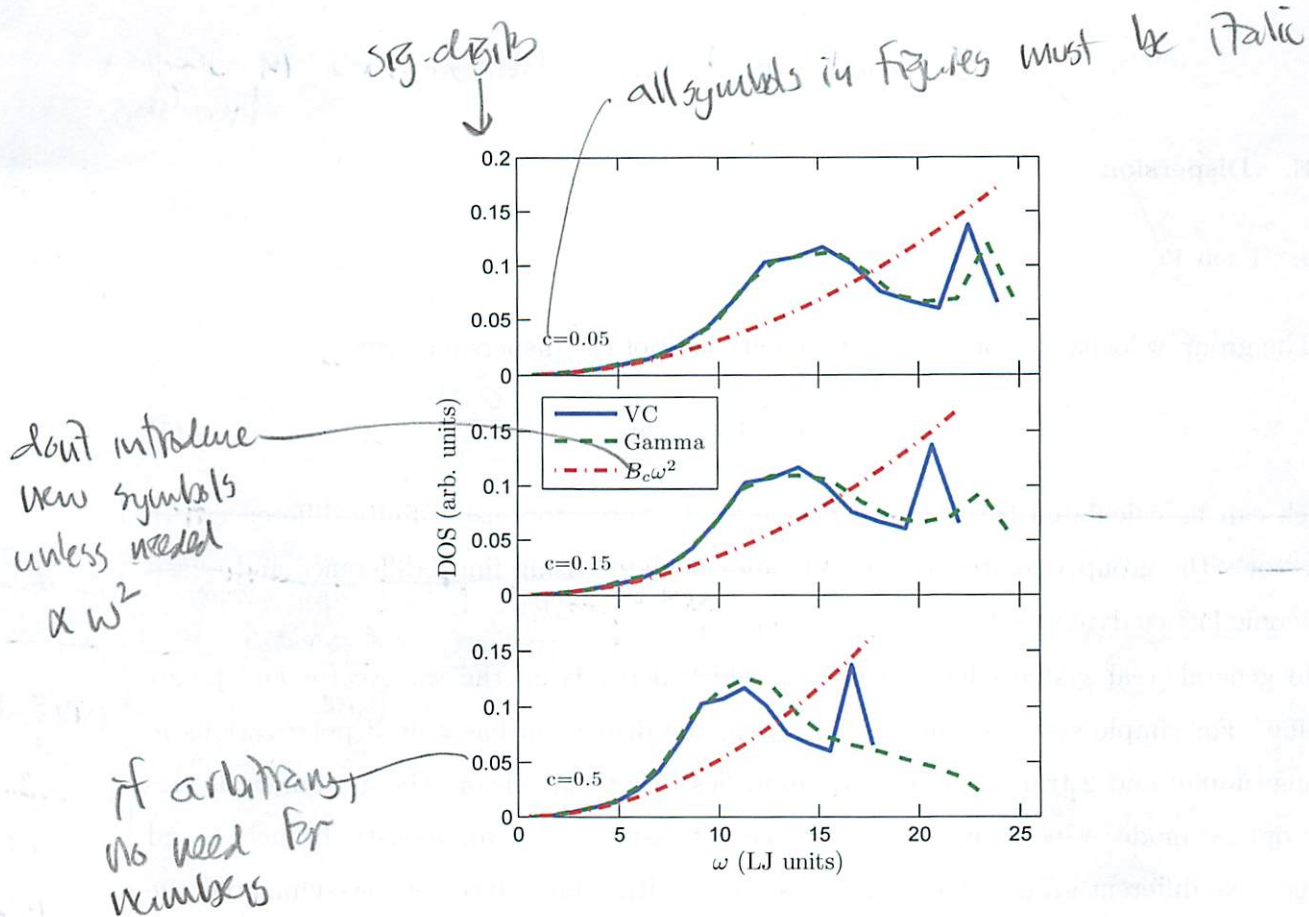- *if arbitrary no need for numbers*

FIG. 2: Density of states (DOS) for modes calculated using the LJ FCC VC versus an explcitily mass disordered LJ FCC supercell (labeled Gamma) with varying mass concentration c (Section). VC and Gamma show similar low frequency behavior for all c. For increasing c, the frequencies of both VC and Gamma decrease, while the high frequency DOS for Gamma spreads and reaches up to a higher maximum frequency because of the explct disorder. The size of these supercells is $N_0 = 12$ (see Section).

dispersion.(cite Mermin)

The increasing lattice mass with increasing *c* for the VC has the effect of reducing the frequencies. The increasing lattice mass for the Gamma modes also has the effect of reducing the frequencies. However, the effect of expicit disorder can be seen at high frequencies by a broadening and a shift of the DOS to higher frequencies because of the explicit use of light atoms in the supercell. Duda et al observed similar high-frequency broadening effects in model LJ alloys.[28] Similar agreement at low frequencies was found in ab initio predictions for Si_cGe_{1-c},[4] while Bouchard showed similar continuous behavior at low frequency for a-Si_cGe_{1-c}.[29]

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E. Dispersion

1. From VC

The group velocity vector in a VC is the gradient of the dispersion curves,

$$v_{g,\mathrm{n}}\left(^{\kappa}_{\nu}\right) = \partial\omega\left(^{\kappa}_{\nu}\right)/\partial\kappa, \qquad \frac{\partial\omega}{\partial|k} \qquad (5)$$

~~which can be calculated from the frequencies and wavevectors using finite differences. In~~ ~~this work,~~ the group velocities for the VC ~~are calculated~~ using finite difference*s* ~~and quasi-~~ harmonic lattice dynamics.[30]

In general, (real) systems have dispersion ~~which~~ depends on the wavevector and polarization. For simple systems, such as LJ argon, the dispersion has ~~only~~ *three* polarizations ν, 1 longitudinal and 2 transverse acoustic branches.[26] For SW silicon, the *two*-atom basis creates optical modes ~~which~~ *that* have distinctly different dispersions than acoustic branches, and hence have different group velocities. For systems with a large basis or low-symmetry, the dispersion can be very complicated.(cite)

Except for the three acoustic branches ~~(2 transverse, 1 logitudinal)~~, there is no~~t~~ an accepted method ~~to~~ *for* predict*ing* the effective group velocity of a vibrational mode in a disordered system, *although* there *have been* ~~are~~ attempts.[21,28,31–33] In the Cahill-Pohl (CP) model, the group velocity of all disordered modes is the sound speed, v_s ~~(Section).~~[31] Dispersion for a model disordered 1D system attributes the reduction of group velocities due to a zone-folding effect.[28] ~~In studies of disordered silicon systems, the group velocity of vibrational modes was estimated using an interpolation scheme for small but finite wavevectors near [000].[21,32,33] footnote (We do not, in general, observe the required dispersion beavhior near the Gamma point to perform the interpolation for the LJ and SW systems studied in this work.[21,32,33])~~

Feldman et al. used the structure factor to predict an effective dispersion for a model of a-Si, but did not predict group velocities.[34] Volz and Chen used the dynamic structure factor to predict the dispersion of *crystalline* SW Si using MD simulation ~~, which is a perfect system~~.[35] As a method to predict mode group velocities, we examine the structure factor for the explicitly disordered modes in the next section.

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2. From Structure Factor of Gamma Modes

Calculating the structure factor of Gamma modes is a method to test for the plane-wave character of disordered modes at a particular wavevector and polarization.[34,36] The structure factor is defined as[36]

$$S^{L,T}(\substack{\kappa \\ \omega}) = \sum_{\nu} E^{L,T}(\substack{\kappa \\ \nu}) \, \delta(\omega - \omega(\substack{\kappa \\ \nu})), \qquad (6)$$

where E^T refers to transverse polarization and is defined as

$$E^{L}(\substack{\kappa \\ \nu}) = \left| \sum_{l,b} \hat{\kappa} \cdot e(\substack{\kappa \ b \\ \nu \ \alpha}) \exp[i\kappa \cdot \mathbf{r}_0(\substack{l \\ b})] \right|^2 \qquad (7)$$

and E^L refers to logitudinal polarization and is defined as

$$E^{T}(\substack{\kappa \\ \nu}) = \left| \sum_{l,b} \hat{\kappa} \times e(\substack{\kappa \ b \\ \nu \ \alpha}) \exp[i\kappa \cdot \mathbf{r}_0(\substack{l \\ b})] \right|^2. \qquad (8)$$

Here, $\mathbf{r}_0(\substack{l \\ b})$ refers to the lattice positions in the mass disordered atoms in the supercells, which are still spaitally ordered. Explicit disorder is accounted for in the mode frequencies $\omega(\substack{\kappa \\ \nu})$ and eigenvectors $e(\substack{\kappa \ b \\ \nu \ \alpha})$, which are calculated with $\hat{\kappa} = [000]$.

Physically, $S^{L,T}(\substack{\kappa \\ \omega})$ calculates the frequency spectrum required to create a wavepacket with well-defined wavevector and polarization.[34,36] The details of the calculation are given in Appendix. For a perfect lattice, the structrue factor peaks are delta functions centered at the phonon mode frequencies, indicating they are pure plane-waves. With increasing disorder, the structure factor spreads in width, particularly at high frequencies because the modes are no longer pure plane-waves. An effective dispersion can be extracted by locating the peaks in the structure factors, where the effects of polarization, virtual mass, and anisotropic dispersion can be observed. As the lattice VC mass becomes larger, the peaks in the structure factor shift to lower frequencies. The peaks in the structure factor are shifted to slightly higher frequencies than the VC predicted frequencies by up to only 5%. Similar good agreement can be seen with the disordered SW silicon lattices, while the structure factors are more complicated because of the optical modes. Because of this good agreement, we use the group velocities predicted by the VC dispersion for both LJ argon and SW silicon with the VC-NMD and VC-ALD calculations for consistency and simplicity (Section and Appendix C). We examine the validity of this choice of group velocity in Section . Well-defined peaks (see Appendix) at all wavevectors are most likely due to the
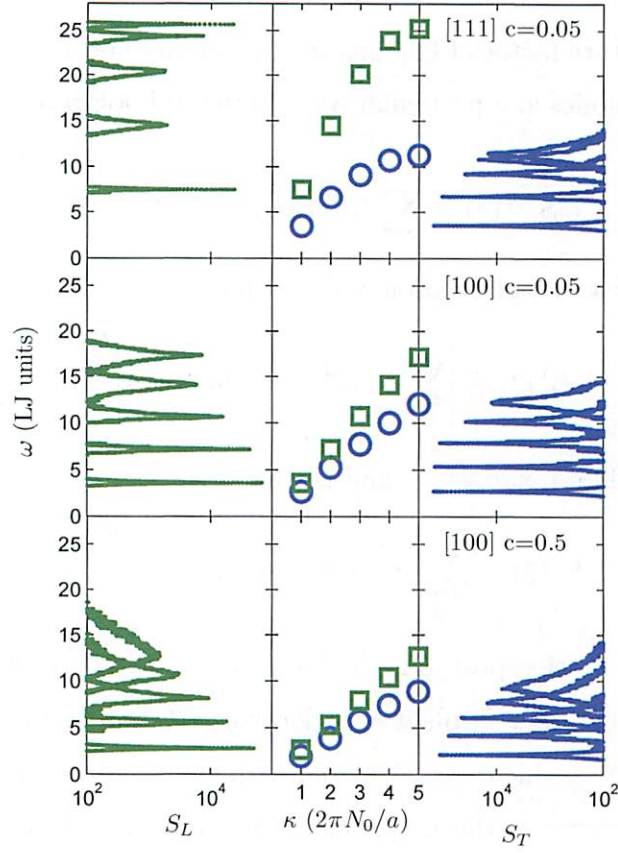
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FIG. 3: Left and Right Panels: The structure factor for logitudinal (S_L) and transverse (S_T) polarizations along high symmetry directions ([100], [110] where $\kappa = \pi/a[100]$ and a is the lattice constant) of the mass disordered LJ FCC supercells ($c = 0.05, 0.5$). For increasing mass disorder c, there is a decrease in the center of the peaks and an increase in the peak linewdiths. Center Panel: The VC predicted dispersion at the same wavevectors used to calculate $S_{L,T}$.

lattice structure of the disordered systems studied in this work. Typically, the structure factor for amorphous materials has well-defined peaks only for small wavevector, which is related to the thermal diffusivity of the disordered modes.[34,36]

I dou't understand

F. Lifetimes

1. From VC-NMD and Gamma-NMD *(which are discussed in the next section)*

As an alternative to the VC-ALD models for predicting phonon lifetimes (Section), we first use the normal mode decomposition (NMD) method.[37,38] NMD maps the atomic trajectories (positions and velocities) of atoms in an MD simulation onto the vibrational normal mode coordinates,(cite)

$$q(^{\kappa}_{\nu}; t) = \sum_{\alpha, b, l}^{3, n, N} \sqrt{\frac{m_b}{N}} u_\alpha(^l_b; t)\, e^*(^{\kappa\ b}_{\nu\ \alpha}) \exp[i\kappa \cdot \mathbf{r}_0(^l_0)] \tag{9}$$

and

$$\dot{q}(^{\kappa}_{\nu}; t) = \sum_{\alpha, b, l}^{3, n, N} \sqrt{\frac{m_b}{N}} \dot{u}_\alpha(^l_b; t)\, e^*(^{\kappa\ b}_{\nu\ \alpha}) \exp[i\kappa \cdot \mathbf{r}_0(^l_0)]. \tag{10}$$

where $\mathbf{r}_0(^l_0)$ are the equilibrium positions of the atoms in the lth unit cell of the lattice supercell under the VC approximation. (needs work) The total energy of a given vibrational mode is given by

$$E(^{\kappa}_{\nu}; t) = \frac{\omega(^{\kappa}_{\nu})}{2} q(^{\kappa}_{\nu}; t)^* q(^{\kappa}_{\nu}; t) + \frac{1}{2} \dot{q}(^{\kappa}_{\nu}; t)^* \dot{q}(^{\kappa}_{\nu}; t). \tag{11}$$

The MD simulation is performed using the perfect and disordered supercells (Section, Fig.). We perform the NMD is performed using the frequencies and eigenvectors from both the VC ($\omega(^{\kappa}_{\nu})$, $e(^{\kappa\ b}_{\nu\ \alpha})$) and the Gamma supercell ($\omega(^{\kappa}_{\nu})$, $e(^{\kappa\ b}_{\nu\ \alpha})$) with $\kappa = [000]$, Section). The vibrational mode frequencies and eigenvectors are necessary for the mapping of the atomic trajectories from the MD simulation onto the vibrational normal mode coordinates, $q(^{\kappa}_{\nu}; t)$ and $\dot{q}(^{\kappa}_{\nu}; t)$, which are required to calculate the kinetic, potential, and total ($E(^{\kappa}_{\nu})(t)$) vibrational normal mode energies.(cite) The effects of disorder enter through the trajectories from these MD simulations, which are also used in the GK method (Section).

The normal vibrational mode lifetime is predicted using

$$\tau(^{\kappa}_{\nu}) = \int_0^{\infty T} \frac{< E(^{\kappa}_{\nu}; t)\, E(^{\kappa}_{\nu}; 0) >}{< E(^{\kappa}_{\nu}; 0)\, E(^{\kappa}_{\nu}; 0) >} dt, \tag{12}$$

where the upper indefinite integral from limit is replaced by a finite set integration given the specifications of the MD simulation. REF This method for predicting the mode lifetime^s is more robust than other

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methods for the disordered systems studied in this work (see Appendix B). It does, however, make it more difficult to predict a phonon frequency, so we use the VC predicted frequency for all VC-NMD predictions, which allow for easier comparison to VC-ALD (Section). *For what system?*

The lifetimes predicted using VC-NMD and Gamma-NMD are shown in Fig. First, the range of frequencies of the modes for VC-NMD and Gamma-NMD differ ~~slightly, particularly at high frequency~~, which is due to ~~the~~ difference in the DOS (Fig.). For small intervals of frequency, there are a wider range of predicted lifetimes for Gamma-NMD. This is because there is no symmetry averaging of the mode properties, which is *possible for the* ~~performed for the modes of VC-NMD given that a~~ VC ~~is assumed~~.(cite)

Lifetimes predicted by both VC-NMD and Gamma-NMD show scalings ~~with frequency~~ *frequency* ~~which are~~ predicted by the perturbative methods of VC-ALD (Section), in particular scalings of ω^{-2}, ω^{-4} and even faster scaling due to the DOS behavior (Fig. , Section). What is not predicted by the perturbative VC-ALD methods is the behavior at the highest frequencies, where τ constant, which is seen roughly for both VC-NMD and Gamma-NMD, except at $c = 0.5$ for VC-NMD. In general, the lifetimes predicted by both VC-NMD and Gamma-NMD are larger than the Ioffe-Regel (IR) limit,[39]

$$\tau = 2\pi/\omega. \qquad \frac{2\pi}{\omega} \qquad (13)$$

The physical interpretation of the IR limit is that of a mode ~~which~~ *that* scatters in a time less than its oscillation period, which is satisfied for most modes in Fig. At the highest frequencies, the existence of this characteristic (thought not exactly minimum) lifetime for LJ argon is analagous to the minimum mean free path used in a simple models of glasses.[40] There is, however, no theoretical prediction of this high-frequency behavior.

While it is possible to predict a MFP given the VC predicted group velocities and the lifetimes predicted by VC-NMD, we find that it is not useful to understanding this high-frequency beavhior. For the group velocities predicted from the VC dispersion, they generally trend towards 0 as the wavevector is increased to the BZ boundaries. This would predict a MFP of 0, which is not helpful to the current discussion. Furthermore, the concept of a MFP becomes poorly defined the more the system is disordered (e.g. dilute alloys to high concentration and amorphous phases). It is thus more useful to consider the proposed lower-limit of the mode thermal diffusivities, which combine the mode lifetime and effective group velocity, or equivalenty, effective MFP (Section).
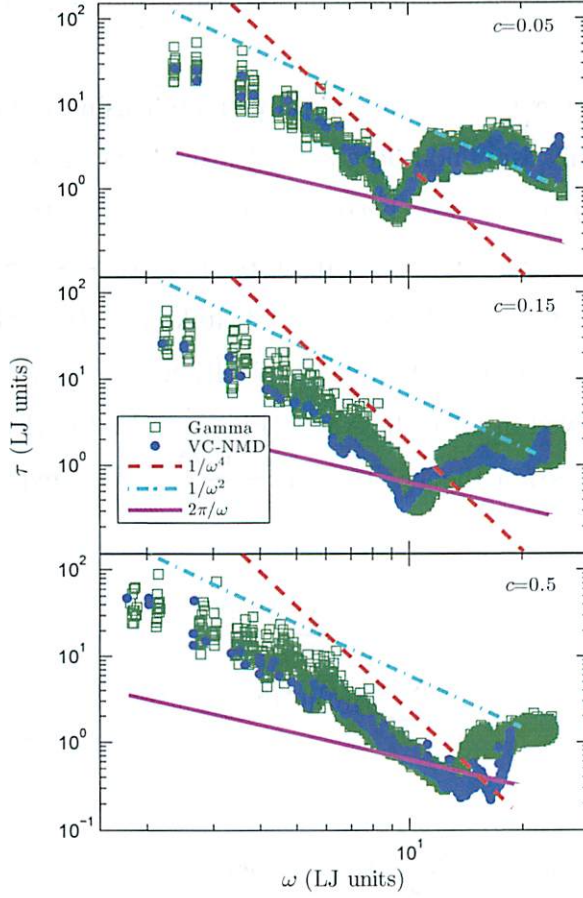
FIG. 4: Lifetimes predicted using VC-NMD and Gamma NMD from MD simulations of mass disordered lattice supercells (Section). Both ω^{-2} and ω^{-4} scalings can be observed at low frequencies, which are predicted by the peturbative models used for VC-ALD (Section). For both VC-NMD and Gamma NMD, most mode lifetimes are greater than the Ioffe-Regel limit $\tau = 2\pi/\omega$.[39] While there is more "noise" in the Gamma mode data (Section), the lifetime magnitudes and trends agree well, an important consideration when comparing VC-NMD and VC-ALD in Fig. .

2. From VC-ALD

Assuming initrinsic and disorder scattering mechanisms to operate independently, the effective phonon lifetime can be found using Matthiessen's rule(cite),

$$\frac{1}{\tau\binom{\kappa}{\nu}} = \frac{1}{\tau_{p-p}\binom{\kappa}{\nu}} + \frac{1}{\tau_d\binom{\kappa}{\nu}}, \tag{14}$$

τ_{p-d}

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where $\tau_{p-p}(^{\kappa}_{\nu})$ accounts for intrinsic phonon-phonon scattering and $\tau_d(^{\kappa}_{\nu})$ accounts for defect scattering.

Phonon-phonon scattering $(\tau_{p-p}(^{\kappa}_{\nu}))$ is typically treated using anharmonic perturbation theory (ALD) including only 3-phonon processes.[1,4,38] It has been demonstrated that the effects of higher order phonon processes become important at high temperatures (see Section).[38,41] At low frequencies where the density of states is Debye-like (Fig.), $\tau_{p-p}(^{\kappa}_{\nu})$ follows a scaling due to both normal $(B_1\omega^{-2})$ and umklapp $(B_2\omega^{-2})$ 3-phonon scattering processes, where the constants B_1 and B_2 are typically fit to experimental data.(cite) The scaling $(\tau \omega^{-2})$ can be observed in both the NMD (Fig.) and ALD (Fig.) predicted results.

Using harmonic perturbation theory, Tamura derives a general expression for mass point defect scattering[11]

$$\frac{1}{\tau_d(^{\kappa}_{\nu})} = \frac{\pi}{2N}\omega^2(^{\kappa}_{\nu}) \sum_{\kappa'\nu'} \delta(\omega(^{\kappa}_{\nu}) - \omega(^{\kappa'}_{\nu'}))$$
$$\sum_b g_2(b)|e^*(^{\kappa'\ b}_{\nu'\ \alpha}) \cdot e(^{\kappa\ b}_{\nu\ \alpha})|^2,$$

(15)

where

$$g_n(b) = \sum_\mu c^\mu(b)(1 - m^\mu(b)/\bar{m}(b))^n,$$ (16)

N is the number of unit cells, and c^μ is the concentration, $m^\mu(b)$ is the mass of the μ-th species and $\bar{m}^\mu$ is the average mass. For the binary LJ argon and SW silicon alloys considered, there is one atom type in the unit cell with $\mu = a, b$, so that the alloying atom labeled by m^b_{1-c} can be considered to be an "isotope" of atom labeled m^a_c. This convention is appropriate because of the perturbative approach used to derive Eq. , while we consider large disorder up to $c = 0.5$.[11]

The term $g_2(b)$ is a coupling term which defines the strength of the disorder which depends on the concentration and masses of the different species. (Give values of g for LJ and SW, at all $c =$ they are approimxately the same given the similar mass ratios used, so that the underprediction of VC-ALD for LJ argon is because of the nature of the system.)

needs work above

Bond disorder can be accounted for using a similar expression with an average atomic radius or suitable scattering cross-section.[42,43] The effect of bond and mass disorder has been investigated computationally by Skye and Schelling for Si/Ge[44], where it was shown that

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