

# Evaluation of the Virtual Crystal Approximation for Predicting Thermal Conductivity

Jason M. Larkin<sup>1</sup> and A. J. H. McGaughey<sup>2,\*</sup>

<sup>1</sup>*Department of Mechanical Engineering  
Carnegie Mellon University  
Pittsburgh, PA 15213*

<sup>2</sup>*Department of Mechanical Engineering  
Carnegie Mellon University  
Pittsburgh, PA 15213*

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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 and thermal conductivity are precited. These two alloyed 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 which treat the disorder explicitly.

## I. INTRODUCTION

Accurately predicting the thermal conductivity of a dielectric or semiconducting material requires the properties of phonons from the entire Brillouin zone. Accurate predictions of phonon properties for bulk systems can be made with anharmonic lattice dynamics (ALD) theory using ab initio calculations.<sup>1–7</sup> However, computational costs limit the size of computational cells in ab initio calculations to be less than 100 atoms, making it difficult to directly incorporate the effects of disorder.<sup>2,3,5,8,9</sup>

Recently, work using ab-initio calculations, anharmonic lattice dynamics (ALD) and the virtual crystal (VC) approximation was used to predict phonon mode frequencies, lifetimes and group velocities of defected materials with realtively large<sup>2,3</sup> and small<sup>5</sup> thermal conductivities. Under this approximation, the disordered crystal is replaced with a perfect virtual crystal with properties equivalent to an averaging over the disorder (e.g. mass or bond strength).<sup>10</sup> The use of ALD with VC (referred to herein as VC-ALD) bases calculations on a small unit cell and treats the effects of intrinsic and disorder scattering as perturbations rather than including disorder explicitly.<sup>5,10,11</sup> However, no comprehensive study has been performed to assess the applicability of this perturbative approach for a range of disorder using multiple predictive methods.

In intro, mention taud model, VC vs. Gamma point, NMD technique.

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 3 predictive methods: MD-based normal mode decomposition (NMD, Section ) and green-kubo (GK, Section ?? ), and VC-ALD which treats the harmonic and anharmonic phonon scattering as perturbations (Section II E 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.

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.

## II. VIRTUAL CRYSTAL (VC) APPROXIMATION

### A. Overview

Abeles first introduced the idea of using a virtual crystal (VC) to replace a disordered one, computing the thermal conductivity of Si/Ge alloys by treating both disorder and anharmonicity as perturbations.<sup>10</sup> 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 and Si/Ge alloys is partly explained by both the increased mass and decreased bulk modulus (stiffness) of

the lattice.(cite) Both have the effect of reducing phonon group velocities. (cite) However, a complete description of the thermal transpot in alloys requires modeling intrinsic and disordered scattering to calculate phonon lifetimes (see Section II E 2).

Phonon lifetimes can be predicted by treating both the intrinsic and disorder scattering using perturbation theory (Section ). While the theory which 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 conductivity reduction in dilute Ge-doped Si epitaxial layers is captured by mass perturbative disorder.<sup>12,13</sup> Even in the case of  $Ni_{0.55}Pd_{0.45}$ , with large mass disorder and concentration ( $m_{Pd}/m_{Ni} \approx 2$ ,  $g = 0.078$  Section ), good agreement is also seen using a VC approach.<sup>14</sup>

Computational results using the VC approximation for high thermal conductivity alloys show good to excellent agreement with experimental results<sup>2,3</sup>. 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.<sup>3</sup> Lindsay and Broido found good agreement with VC-ALD and experiment for isotopically defected GaN.<sup>2</sup> Both Si/Ge alloys and isotopically defected GaN have relatively large thermal conductivities, even for large concentrations.(cite) A detailed study of low thermal conductivity materials PbTe<sup>4</sup> and PbTe/PbSe<sup>5</sup> made predictions for the perfect systems in fair agreement with experiment, where results lack for the alloys. 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.

needs work

Using computationally-cheap empirical potentials for argon and silicon<sup>15</sup>, we study the effects of disorder explicitly. Using the VC approximation, we perform calculations at different concentrations ( $c$ ) of mass varying ( $m_1^a m_c^b$ ) binary alloys of LJ argon and SW 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 ),<sup>16</sup> and molecular dynamics (MD) simulations (Section ).

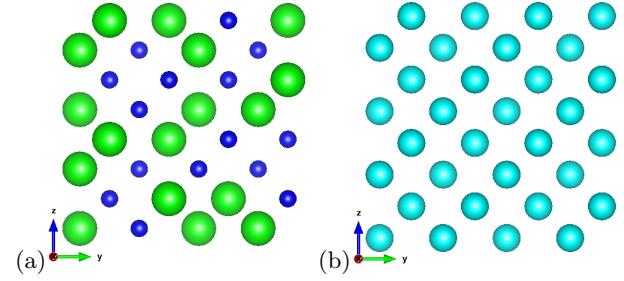


FIG. 1: (a) view of a [010][001] plane of an explicitly disordered supercell of Si and ‘heavy’ Si ([100] direction into the paper).<sup>17</sup> (b) view of a [010][001] plane of the VC supercell with an average mass of the explicitly disordered Si and ‘heavy’ Si supercell (b). Sphere size represents 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 II C, II D 1, II E 1 and II E 2), which build the lattice of the perfect (a) and disordered supercells (b). Disorder is taken into account explicitly using the disordered supercells in Sections II C, II D 2, II E 1 and ??.

## B. Kinetic Theory or Thermal Conductivity Models

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<sup>18</sup> as an approximate solution of the Boltzmann transport equation<sup>19</sup> gives an expression for thermal conductivity,

$$k_{ph,\mathbf{n}} = \sum_{\boldsymbol{\kappa}} \sum_{\nu} c_{ph}(\boldsymbol{\kappa}) \mathbf{v}_{g,\mathbf{n}}^2(\boldsymbol{\kappa}) \tau(\boldsymbol{\kappa}). \quad (1)$$

Here, the phonon mode has frequency  $\omega(\boldsymbol{\kappa})$  (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  $\tau(\boldsymbol{\kappa})$  is the phonon lifetime (Section ). Since the MD simuilations we perform (Section ) are classical and obey Maxwell-Boltzmann statistics,<sup>20</sup> 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. (cite SED or AMSE?) For the perfect and disordered lattices studied in this work, the thermal conductivity is isotropic, so we refer to  $k_{ph}$  only.

For disordered systems, the Allen-Feldman (AF) theory computes the contribution to vibrational conductivity by diffuson modes (Section ).<sup>16</sup> In the AF theory, disordered vibrational modes are defined at the wavevector [000] (referred to as Gamma, Section ) and couple harmonically to produce a mode thermal diffusivity (Section ). The relative contribution of both

phonons and diffusons to the total vibrational conductivity,  $k_{vib} = k_{ph} + k_{AF}$ , has been estimated for amorphous silicon.<sup>21</sup> In the current study of disordered lattices, the AF theory provides 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 ).

### C. VC and Gamma DOS

In this section, we examine the effect of explicit disorder by computing the density of states (DOS,  $D(\omega(\kappa))$ ) for vibrational modes of and of explicitly mass disordered lattice supercells and their equivalent VCs. 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.(cite) 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  $N_0 \leq 12$  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  $N_0 \leq 24$  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  $m_{1-c}^a m_c^b$ , where  $m^a = 1$  and  $m^b = 3$  in LJ units for argon and  $m^a = m_{Si}$  and  $m^b = 2.6m_{Si}$  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  $a = 1.580$  (T=40 K) in LJ units.<sup>22</sup> 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 ( $a = 1.585$ ).<sup>22</sup> All LJ calculations use these lattice constants. For SW silicon, the lattice constant  $a = 5.43\text{\AA}$  is used for all calculations, which brings the GK thermal conductivity predictions<sup>23</sup> into better agreement with VC-ALD<sup>24</sup> for  $c = 0.0$  (Section ).

Each vibrational mode contributing to the thermal conductivity has a frequency  $\omega(\kappa)$ . The allowed frequencies are the square root of the eigenvalues of the system's Dynamical matrix,  $D(\kappa)$ ,<sup>25</sup> which relates the normal mode eigenvector ( $e(\kappa \alpha)$ ) and eigenvalue by

$$D(\kappa)e(\kappa \alpha) = \omega^2(\kappa) e(\kappa \alpha). \quad (2)$$

The set of eigenvalues and eigenvectors are the orthonormal basis of the vibrational lattice.<sup>25</sup> In a perfect system all vibrational (normal) modes are plane-waves, and as such can be identified by a wave-vector  $\kappa$ , eigenvector  $e(\kappa \alpha)$ , and a possibly degenerate frequency  $\omega(\kappa)$ . Here,  $b$  labels the atom in the unit cell,  $\alpha$  labels the cartesian

coordinates, and  $\nu$  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. 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 .

With the appropriate dynamical matrix ( $\kappa = [000]$  for the explicitly disordered lattice supercells), the frequencies are computed using the program GULP.<sup>26</sup> For the VC, the frequencies are identified (up to polarization) by the list of wavevectors allowed by the size of the 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 frequencies, where the Debye approximation predicts  $DOS(\omega) \propto \omega^2$ .(cite) The Debye approximation under-predicts the DOS at moderate frequency, which is due to the non-linear 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 explicit 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. Similar agreement at low frequencies was found in ab initio predictions for  $Si_cGe_{1-c}$ ,<sup>3</sup> while Bouchard showed similar continuous behavior at low frequency for for a- $Si_cGe_{1-c}$ .<sup>27</sup> Duda et al observed similar high-frequency broadening effects in model LJ alloys.<sup>28</sup>

### D. Phonon Group Velocities

#### 1. From VC Dispersion

The group velocity vector in a VC is the gradient of the dispersion curves (i.e.,  $\partial\omega/\partial\kappa$ ), 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 and quasi-harmonic lattice dynamics.<sup>29</sup> While the group velocities are necessary to predict the thermal conductivity, of particular interest is the phonon mean free path (MFP),  $\Lambda(\kappa) = |\mathbf{v}_g| \tau(\kappa)$ , which is crucial for understanding nano and micro-nanostructuring effects.(cite) Predicting group velocities in disordered systems is just as crucial as predicting mode lifetimes.

Sound speeds of alloys: can't find any good references.

In general, real systems have dispersion such that  $v_g(\kappa)(\omega(\kappa))$ . For simple systems, such as LJ argon, the dispersion has only 3 polarizations  $\nu$ , 1 longitudinal and 2 transverse acoustic branches.<sup>25</sup> For SW silicon, the 2-atom basis creates optical modes which have distinctly

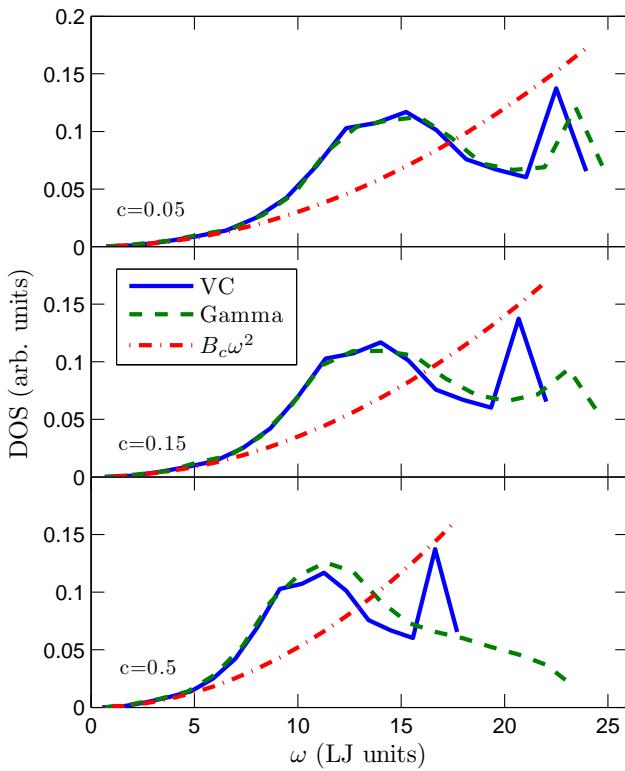


FIG. 2: Density of states (DOS) for modes calculated using the LJ FCC VC versus an explicitly mass disordered LJ FCC supercell (labeled Gamma) with varying mass concentration  $c$  (Section ). VC and Gamma show similar low frequency behavior for all  $c$ . For increasing  $c$ , the frequencies of both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

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 longitudinal), there is not an accepted method to calculate the effective group velocity of a vibrational mode in a disordered system, though there are attempts.<sup>21,28,30–32</sup> In the Cahill-Pohl (CP) model, the group velocity of all disordered modes is  $v_s$  (Section ).<sup>30</sup> Dispersion for a model disordered 1D system attributes the reduction of group velocities due to a zone-folding effect.<sup>28</sup> 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].<sup>21,31,32</sup> footnot (We do not, in general, observe the required dispersion beavhior to perform this interpolation for the LJ and SW systems studied in this work.)

Feldman et al used the structure factor to predict an effective dispersion for a model of a-Si, but did not pre-

dict group velocities.<sup>33</sup> Volz and Chen used the dynamic structure factor to predict the dispersion of SW Si using MD simulation, which is a perfect system.<sup>34</sup> As a method to predict mode group velocities, we examine the structure factor for the explicitly disordered modes in the next section.

## 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.<sup>33,35</sup> The structure factor is defined as<sup>35</sup>

$$S^{L,T}(\kappa) = \sum_{\nu} E^{L,T}(\nu) \delta(\omega - \omega(\nu)), \quad (3)$$

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

$$E^L(\nu) = \left| \sum_{l,b} \hat{\kappa} \cdot e(\nu \alpha) \exp[i\kappa \cdot \mathbf{r}_0(l)] \right|^2 \quad (4)$$

and  $E^L$  refers to longitudinal polarization and is defined as

$$E^T(\nu) = \left| \sum_{l,b} \hat{\kappa} \times e(\nu \alpha) \exp[i\kappa \cdot \mathbf{r}_0(l)] \right|^2. \quad (5)$$

Here,  $\mathbf{r}_0(l)$  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  $\omega(\nu)$  and eigenvectors  $e(\nu \alpha)$  which are calculated with  $\kappa = [000]$ .

Physically,  $S^{L,T}(\kappa)$  calculates the frequency spectrum required to create a wavepacket with well-defined wavevector and polarization.<sup>33,35</sup> For a perfect lattice, the structre factor peaks are delta functions centered at the phonon mode frequencies.(DIFFERENTIATE BETWEEN PLANE-WAVE AND DISORDERED MODE) With increasing disorder ( $c$ ), the structure factor spreads in width, particularly at high frequencies (Fig ). 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 (Fig. ). 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 %. Similar good agreement can be seen with SW silicon. Because of this, 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 ). Well-defined peaks at all wavevectors are most likely due to the lattice structure of the disordered

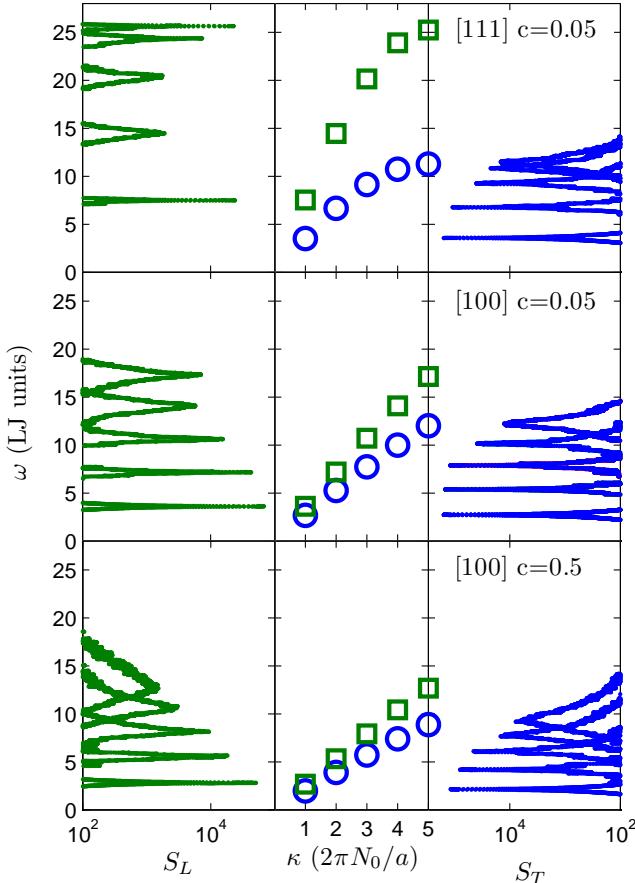


FIG. 3: Left and Right Panels: The structure factor for longitudinal ( $S_L$ ) and transverse ( $S_T$ ) polarizations along high symmetry directions ([100], [110] where  $\kappa = \pi/a[100]$  and  $a$  is the lattice constant ) of the mass disordered LJ FCC supercells ( $c = 0.05, 0.5$ ). For increasing mass disorder  $c$ , there is a decrease in the center of the peaks and an increase in the peak linewidths. Center Panel: The VC predicted dispersion at the same wavectors used to calculate  $S_{L,T}$ .

systems studied in this work. Typically, the structure factor for amorphous materials has well-defined peaks only for small wavevector.<sup>33,35</sup>

### E. Phonon Lifetimes

#### 1. From VC-NMD and Gamma

As an alternative to the VC-ALD models for predicting phonon lifetimes (Section ), we use the normal mode decomposition (NMD) method.<sup>36,37</sup> NMD maps the atomic trajectories (positions and velocities) of atoms in an MD simulation onto vibrational normal modes.(cite) The MD simulation is performed using the perfect and disordered supercells (Section , Fig. ). The NMD is performed us-

ing the frequencies and eigenvectors from both the VC ( $(\omega_\nu^\kappa, e_\nu^\kappa)$ ,  $e_\nu^\kappa$ ) and the Gamma supercell ( $(\omega_\nu^\kappa, e_\nu^\kappa)$  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 for the GK method (Section ).

The normal mode lifetime is predicted using

$$\tau(\kappa_\nu) = \int_0^\infty \frac{\langle E(\kappa_\nu; t) E(\kappa_\nu; 0) \rangle}{\langle E(\kappa_\nu; 0) E(\kappa_\nu; 0) \rangle} dt, \quad (6)$$

where the indefinite integral is replaced by a finite integration given the specifications of the MD simulation. This method for predicting the mode lifetime is more robust than other 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 ).

The lifetimes predicted using the VC-NMD 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 performed for the modes of VC-NMD given that a VC is assumed.(cite)

Overall, the lifetimes predicted by both VC-NMD and Gamma-NMD are larger than the Ioffe-Regel limit ( $\tau = 2\pi/\omega$ , Fig. ).<sup>38</sup> Lifetimes predicted by both VC-NMD and Gamma-NMD show scalings with frequency which are predicted by the perturbative methods of VC-ALD (Section ), in particular scalings of  $\omega^{-2}$ ,  $\omega^{-4}$  and even faster scaling due to the DOS behavior (Section ). What is not predicted by the perturbative VC-ALD methods is the behavior at the highest frequencies, where  $\tau$  constant, which is seen roughly for both VC-NMD and Gamma-NMD, except at  $c = 0.5$  for VC-NMD. The existence of this characteristic (thought not exactly minimum) lifetime for LJ argon is analogous to the minimum mean free path used in a simple model of glasses.<sup>39</sup>

#### 2. From VC-ALD

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

$$\frac{1}{\tau(\kappa)} = \frac{1}{\tau_{p-p}(\kappa)} + \frac{1}{\tau_d(\kappa)}, \quad (7)$$

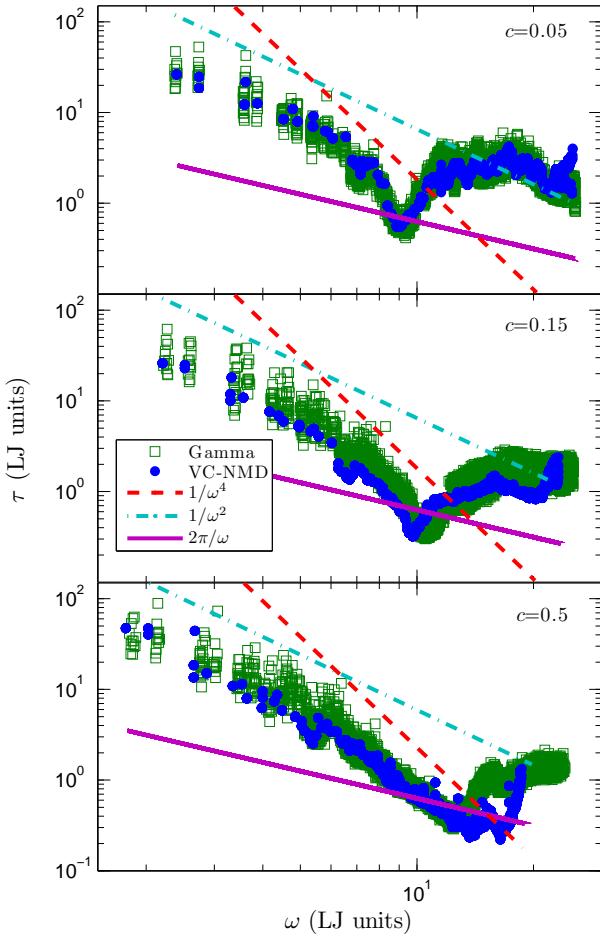


FIG. 4: Lifetimes predicted using VC-NMD and Gamma NMD from MD simulations of mass disordered FCC supercells (Section ). Both  $\omega^{-2}$  and  $\omega^{-4}$  scalings can be observed at low frequencies, which are predicted by the perturbative models used for VC-ALD (Section ). For both VC-NMD and Gamma NMD, most mode lifetimes are greater than the Ioffe-Regel limit  $\tau = 2\pi/\omega$ .<sup>38</sup> While there is more “noise” in the Gamma mode data because of the symmetry averaging of the VC-NMD modes (Section ), the lifetime magnitudes and trends agree well, an important consideration when comparing VC-NMD and VC-ALD in Fig. .

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

Phonon-phonon scattering ( $\tau_{p-p}(\kappa)$ ) is typically treated using anharmonic perturbation theory (ALD) including only 3-phonon processes.<sup>3,5,37</sup> It has been demonstrated that the effects of higher order n-phonon processes become important at high temperatures (see Section ).<sup>37,40</sup> At low frequencies where the density of states is Debye-like (Section Fig. ),  $\tau_{p-p}(\kappa)$  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 scal-

ing  $\tau \omega^{-2}$  can be observed in both the NMD (Fig. ) and ALD (Fig. ) predicted results.

Using harmonic perturbation theory, Tamura gives a general expression for mass point defect scattering<sup>11</sup>

$$\frac{1}{\tau_d(\kappa)} = \frac{\pi}{2N} \omega^2(\kappa) \sum_{\kappa' \nu'} \delta(\omega(\kappa') - \omega(\kappa')) \sum_b g(b) |e^*(\kappa' \nu') \cdot e(\kappa \nu)|^2, \quad (8)$$

where  $g(b) = \sum_\mu c^\mu(b)(1 - m^\mu(b)/\bar{m}(b))^2$ ,  $N$  is the number of unit cells, and  $c^\mu$  is the concentration,  $m^\mu(b)$  is the mass of the  $\mu$ -th species and  $\bar{m}$  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  $m_{1-c}^b$  can be considered to be an “isotope” of atom labeled  $m_c^a$ . This convention is appropriate because of the perturbative approach used to derive Eq. , while we consider large disorder of up to  $c = 0.5$ .<sup>11</sup> (Give values of  $g$  for LJ and SW, at all  $c =$  they are approximately 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.)

Bond disorder can be accounted for using a similar expression with an average atomic radius or suitable scattering cross-section.<sup>41,42</sup> The effect of bond and mass disorder has been investigated computationally by Skye and Schelling for Si/Ge<sup>43</sup>, where it was shown that mass disorder is the dominant scattering mechanism. In this work we consider only mass disorder.

By considering the symmetry properties of the FCC lattices considered in this work (Section ), it can be shown that  $1/\tau_d(\kappa) = \frac{\pi}{2} g \omega^2(\kappa) D(\omega(\kappa))$ , where  $D(\omega(\kappa))$  is the density of states (Section ).<sup>11</sup> Under the Debye-approximation ( $D(\omega(\kappa)) \propto \omega^2$ ), the phonon scattering due to mass point-defects is given by  $A\omega^{-4}$ , where  $A$  is a constant related to the unit cell volume, branch-averaged group velocity, and disorder coupling strength ( $g$  in Eq. above). The frequency dependence ( $\omega^4$ ) is the same as Rayleigh scattering, which is valid at low frequency and observed in both the NMD (Fig. ) and ALD (Fig. ) predicted results. The disorder scattering scaling is expected to fall off faster than  $\omega^{-4}$  when  $D(\omega(\kappa))$  grows faster than the Debye scaling of  $\omega^2$  (Fig. , Section ). The lifetimes do fall off faster  $\omega^{-4}$  for the mass disordered LJ FCC supercells for a narrow range of frequencies near  $\omega = 10$  in Fig. for  $c = 0.05, 0.15$ , but seem to follow more closely  $\omega^{-4}$  for  $c = 0.5$ .

For the VC-ALD method, the intrinsic  $\tau_{p-p}(\kappa)$  is calculated using the method described in<sup>37</sup>, using all classical expressions to remain consistent with the classical MD-based methods NMD and GK (Section ). To calculate the disordered lifetimes  $\tau_d(\kappa)$  (Eq. ), it is necessary to broaden the  $\delta$  function using afootnote[1] Lorentzian function. For all calculations, the Lorentzian was broadened using a value of  $100\delta_{\omega,avg}$  (Section ). For the system sizes here, the results do not differ significantly if

this broadening value is varied by changing it manually or making the system size ( $N_0$ ) bigger.

### F. Vibrational Mode Diffusivity

The diffusivity section was a bit hard to follow.

In the classical limit, where the specific heat  $c_p(\kappa) = k_B$ , a vibrational mode's contribution to thermal conductivity is determined by the mode thermal diffusivity. For phonons, the thermal diffusivity is

$$D_{ph}(\omega(\kappa)) = v_g^2(\kappa) \tau(\kappa). \quad (9)$$

We now compare the phonon mode diffusivities,  $D_{ph}(\omega(\kappa))$  predicted by both VC-NMD and VC-ALD to the proposed lower limit  $D_{AF,HS} = (1/3)v_s a$  (see Section ). Here,  $a$  is 1/2 the lattice constant of the cubic conventional unit cells used for both FCC LJ argon and diamond-FCC SW silicon, although the choice of this length scale is not unique. For the a value in Eqs. (12)-(14), why not use the bond length?

For LJ argon, VC-NMD predicts lifetimes which are generally larger than the period ( $2\pi/\omega(\kappa)$ ) of the vibrational oscillation (Ioffe-Regel limit)(cite), and actually increase high frequency for small intervals (Fig. and ). VC-NMD predicts larger phonon lifetimes at high frequency compared to VC-ALD (Fig. ), which predicts essentially monotonically decreasing lifetimes with increasing frequency. Because VC-NMD and VC-ALD use the same values for  $v_g(\kappa)$ , the phonon mode diffusivities  $D_{ph}$  are also underpredicted by VC-ALD compared to VC-NMD. This leads to an underprediction for VC-ALD of both the thermal conductivity spectrum (Fig. ) at high frequency and the total thermal conductivity (Fig. ) compaed to VC-NMD.

For both VC-NMD and VC-ALD, a significant number of modes have  $D_{ph}(t; t) D_{AF,HS}$ . This leads to an underprediction of the total thermal conductivity compared to GK (Fig. ). The diffusivity of these modes can be adjusted such that any mode with  $D_{ph}(t; t) D_{AF,HS}$  is given  $D_{ph} = D_{AF,HS}$ . The result of this adjustment, referred to as VC-NMD\* and VC-ALD\*, is examined in the next section.

The energy diffusivity,  $d$ , quantifies how far a wave packet narrowly peaked at a frequency can propagate.<sup>16,44,45</sup>

A heuristic argument for the relation between  $d$  and  $T$  is as follows. For a system in a temperature gradient, it is well known that the heat diffusivity obeys the relation  $d = V / C$ . Thus,  $= dC / V$ . This relation can be generalized mode by mode.

In amorphous systems, the diffusivities themselves can be combined using a Matthiesen-like expression (multiple resistors in series).<sup>46</sup>

In the AF theory, the mode diffusivities typically diverges as  $\omega - > 0$  because the vibrational modes are long-wavelength plane waves (phonons) that weakly scattered by the disorder.<sup>47</sup> For a finite thermal conduction

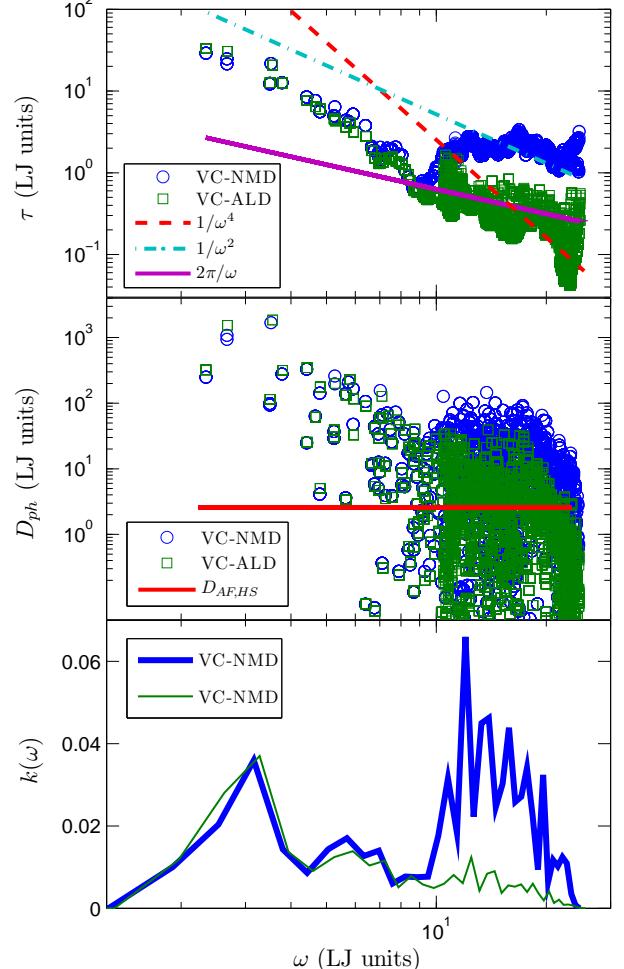


FIG. 5: gamma point results

tivity, the mode diffusivity at low-frequency is of the form  $D_{vib} = (1/3)v_s^2 \tau(\kappa)(\omega(\kappa))$  with  $v_g(\kappa) = v_s(\nu)$  and  $\tau(\kappa) \propto \omega^{-2}$ . There is no known harmonic model which can give this low-frequency result.<sup>33</sup> For the disordered lattices studied in this work for  $c \leq 0.15$ , the  $k_{AF}$  is strongly system size dependent, indicating this diverging behavior. For  $c = 0.5$ , the divergence with system size is small for the range of system size studied ( $N_0 = 4$  to  $N_0 = 12$ ), where  $k_{AF}/k_{GK} = 0.93$  for  $N_0 = 12$ .

The diffusivity  $D_i$  cannot be meaningfully represented as  $v^{2/3}$  since  $v_i$  and  $i$  cannot be independently defined.<sup>33</sup>

<sup>39</sup>

At very low frequency, the mode diffusivities for phonons or diffusons can be factored as the product of the sound speed,  $D_{ph} = v_s^2(\kappa) \tau(\kappa)$  and  $D_{AF} = (1/3)(v_s)^2 \tau_{AF}$ .

The key difference is that for the lattices studied in this work, for  $c = 0$  there is dispersion such that  $v_g(\kappa) \neq v_s$  as in the Cahill-Pohl model. For

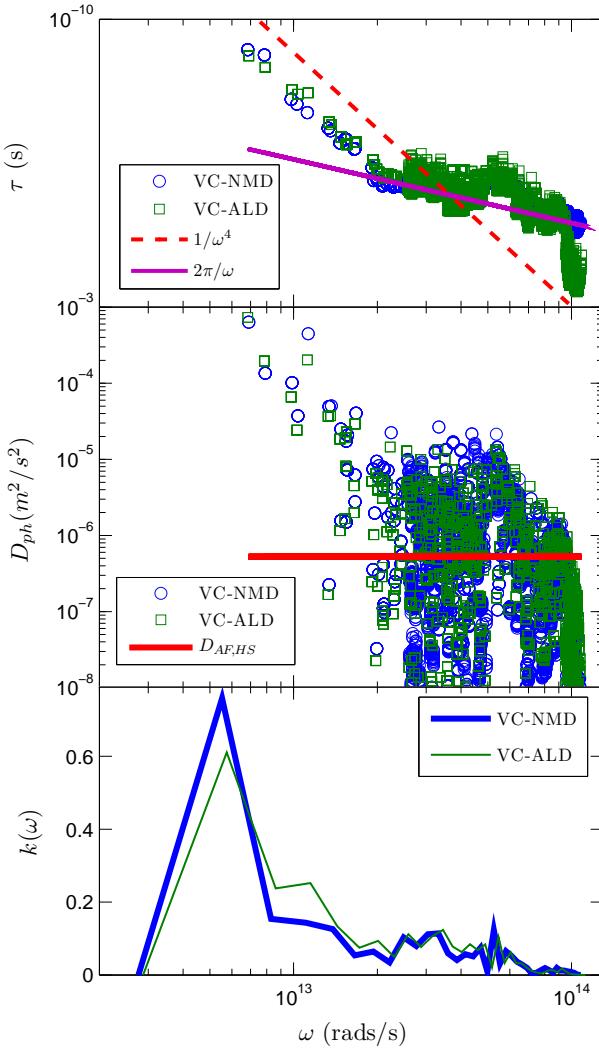


FIG. 6: gamma point results

perturbative disorder ( $c = 0.05$  Fig. ), the narrow peaks of the disordered lattice's structure factor (Section ) suggest that the

This perplexing property of glasses has been explained heuristically by assuming that phonons are scattered so strongly by structural disorder that transport becomes diffusive, with a frequency regime of small, constant thermal diffusivity<sup>48,49</sup>

By contrast,  $T$  is generally infinite if anharmonic corrections are ignored. This is because  $d$  in the integrand of Eq. 4 diverges too strongly at low  $\omega$  due to phonons that are progressively less scattered with increasing wavelength.<sup>45</sup> In order to cure this divergence, additional scattering mechanisms, beyond harmonic theory, are typically invoked resulting in an additional contribution to the diffusivity,  $d_c$

In heavily disordered systems, such as large  $c$  alloys or glasses, modes can transport heat by harmonic coupling due to the disorder in the Allen-Feldman (AF) theory of

diffusons.<sup>16</sup> In the classical limit, the AF thermal conductivity is written as

$$k_{AF} = \sum_{\nu} \frac{k_B}{V} D_{AF}(\omega_{\nu}), \quad (10)$$

where  $V$  is the system volume and  $D_{AF}(\omega_{\nu})$  is the thermal diffusivity of the mode labeled by frequency  $\omega_{\nu}$  with  $\nu$  ranging over all modes in the disordered supercell and  $\kappa = [000]$ .(cite)

In a weakly scattering system,  $D_{AF} = v_s \tau(\omega)/3$ <sup>44</sup> energy transport in jammed sphere packings<sup>44</sup> heat transport in model jammed solids<sup>45</sup>

In fact, for a-Si, the mode diffusivities do vary as a function of frequency,<sup>33,35,50</sup> which has been used to explain the propagating mode effects seen in a-Si thin films. ( $D = v_s \tau$ )<sup>21</sup>

In the high-scatter (HS) limit,(cite) the AF diffusivity of each mode is

$$D_{AF,HS} = \frac{1}{3} v_s a. \quad (11)$$

A similar HS limit for mode diffusivity is given by the Cahill-Pohl (CP) model,(cite)

$$D_{CP,HS} = 0.403 v_s a. \quad (12)$$

The CP thermal conductivity prediction in the HS limit is

$$k_{CP,HS} = \left(\frac{\pi}{6}\right)^{1/3} \left(\frac{3}{2}\right) \frac{k_B}{V_b} b v_s a, \quad (13)$$

where  $V_b$  is the volume of the unit cell,  $v_s$  is the branch-averaged sound speed, and  $a$  is the lattice constant (or appropriate length scale).<sup>30</sup> Comparing with Eq., the AF,HS limit predicts a mode diffusivity and thermal conductivity which is approximately %20 smaller than CP,HS.<sup>30</sup> Ignoring this small difference, the interpretation for both  $D_{AF,HS}$  and  $D_{CP,HS}$  is of a vibrational mode with a group velocity equal to the sound speed and mean-free path equal to the lattice spacing. While the CP,HS model assumes  $\tau(\kappa) = 1/\omega(\kappa)$  and  $v_g = v_s$  for all modes, the AF theory is capable of predicting the mode diffusivities without any assumptions other than a harmonic approximation.(cite)

At the highest frequencies, Feldman et al showed that the thermal diffusivities in a-Si show a sharp breakpoint at the onset of localized states, where it tends to zero exponentially. Similar behavior is seen for the disordered lattices ( $c = 0.5$ , Fig. ), where it can be shown that these states are localized spatially by examining the eigenvector.(cite)

With sufficient disorder, the harmonic AF theory is capable of accurately predicting a finite thermal conductivity.<sup>50,51</sup> However, the AF theory does not treat the intrinsic anharmonic scattering of low frequency phonon modes, where in the infinite-size the AF conductivity of a disordered lattice is divergent.(cite) While the

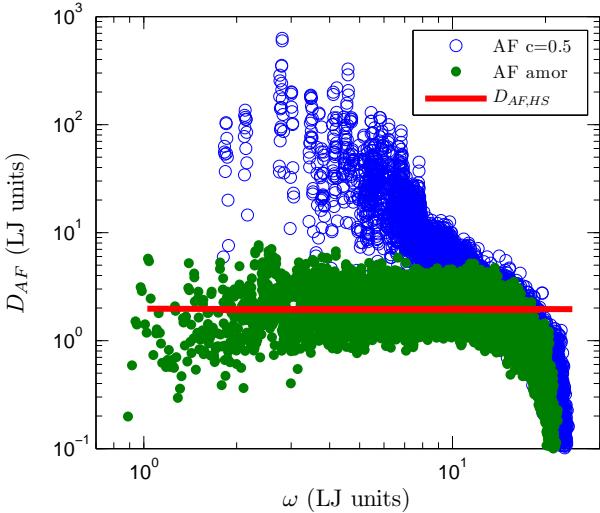


FIG. 7: gamma point results

low frequency modes are not treated properly in the harmonic AF theory, the mode diffusivities  $D_{AF}$  of high frequency modes in the heavily disordered ( $c = 0.5$ ) LJ FCC supercell approach that of similar frequency modes in the amorphous phase (Fig. ).<sup>52</sup> (The amorphous LJ phase was created by liquifying the crystal and instantly quenching by removing all kinetic energy. The resulting structure was then energy minimized and annealed in an NPT ensemble at zero pressure and  $T = 10$  K.) In the amorphous phase, modes with significant contribution to thermal transport can be modeled using a mode-independent diffusivity of  $D_{AF,HS}$  (Eq. ). In fact, the difference between  $k_{AF} = 0.099W/m = K$  and  $k_{HS,CP} = 0.124$  is approximately %20. This places a plausible lower-bound on the value of the phonon mode diffusivities,  $D_{ph} \geq D_{AF,HS}$ , predicted by VC-NMD and VC-ALD in the following section.

### III. THERMAL CONDUCTIVITY PREDICTIONS

An addition of as little as 10% Ge is sufficient to reduce the thermal conductivity to the minimum value achievable through alloying. Theoretically, mass disorder is found to increase the anharmonic scattering of phonons through a modification of their vibration eigenmodes. Notably, the thermal conductivity is found to drop sharply after only a small amount of alloying. This is due to the strong harmonic scattering of phonons even in the dilute alloy limit.

Duda shows that taking a perfect alloy and disordering via an order parameter allows control of thermal conductivity.<sup>52</sup>

In fact, the beginning breakdown of the intrinsic scat-

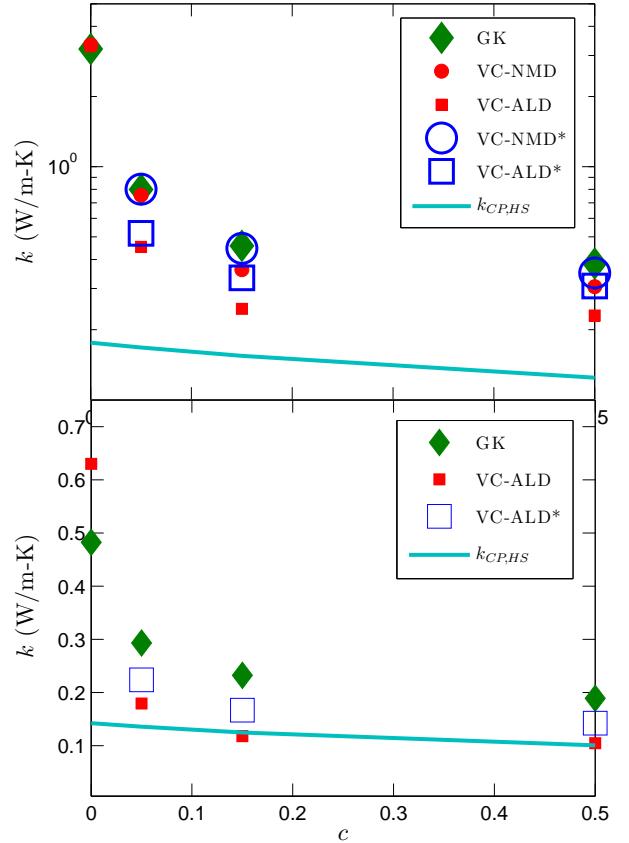


FIG. 8: The vibrational conductivity of LJ alloys predicted using MD simulations and the GK method. The predicted thermal conductivities are for a LJ alloy of the form  $m_{1-c}^a m_c^b$ , where  $m^a = 1$ ,  $m^b = 3$ , and  $m_r = m^a/m^b = 3$  (in LJ units). As the alloy concentration is increased perturbatively, the vibrational conductivity drops quickly and saturates to a minimum at  $c = 0.5$ . For  $c = 0.5$  the system is heavily disordered and the vibrational conductivity approaches that of an amorphous system.

tering model ( $\tau_{p-p}(\omega)$ ) can be observed for the perfect ( $c = 0.0$ ) crystal at  $T = 40$  K (see Fig. ), where ALD begins to overpredict compared to GK. This can be explained by the emerging importance of higher order ( $n > 3$ ) n-phonon process at high temperatures.<sup>37</sup>

For LJ argon, bulk thermal conductivity predictions are made for VC-NMD, VC-ALD and GK (Fig. ). For SW silicon, bulk thermal conductivity predictions can only be made for VC-ALD and GK (see Appendix ). For LJ argon, both VC-NMD and VC-ALD underpredict the thermal conductivity compared to GK. By adjusting the mode diffusivity  $VC - NMD*$  and  $VC - ALD*$ .

### IV. DISCUSSION

The group velocity of moderate to high frequency modes in a 1D alloy are drastically reduced by consid-

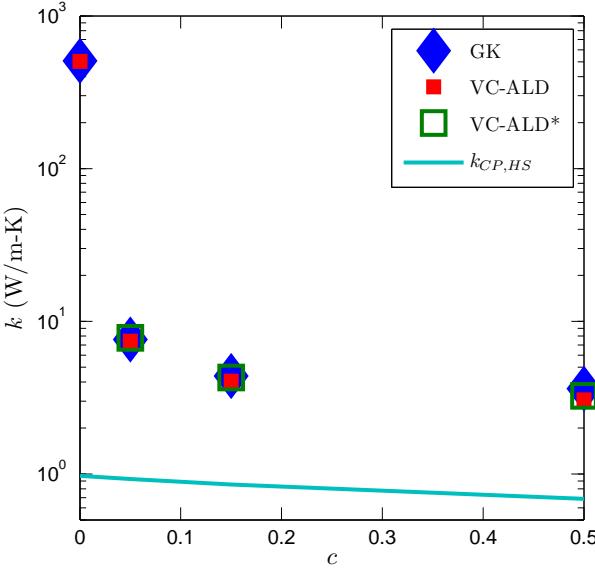


FIG. 9: The vibrational conductivity of LJ alloys predicted using MD simulations and the Green-Kubo method. The predicted thermal conductivities are for a LJ alloy of the form  $m_{1-c}^a m_c^b$ , where  $m^a = 1$ ,  $m^b = 3$ , and  $m_r = m^a/m^b = 3$  (in LJ units). As the alloy concentration is increased perturbatively, the vibrational conductivity drops quickly and saturates to a minimum at  $c = 0.5$ . For  $c = 0.5$  the system is heavily disordered and the vibrational conductivity approaches that of an amorphous system.

ering the effects of zone folding.<sup>28</sup> Based on the results locating the peaks in the structure factors (Fig. ), the reduction due to zone folding would seem to underpredict the group velocity of moderate to high frequency modes. This ambiguity can be resolved by considering the thermal diffusivity of a given mode, which incorporates the variation of both group velocity and lifetime (see Section ).

While there is a clear breakdown of the perturbative models used in VC-ALD (Fig. LJ-Diff and Fig. LJ thermal cond 40K), Because of its computational efficiency (Appendix ) a simple correction VC-ALD\* is useful. This correction brings the predictions for LJ argon into better (though not great) agreement with the MD-based methods, and does not affect the good agreement seen in SW silicon (Fig. ).

The existence of a minimum or characteristic mode lifetime for LJ argon (Fig. ) can be . Such a minimum, defined in terms of the mode mean free path was, was proposed to explain the plateau temperature dependence of glasses.<sup>39</sup> There is difficulty in converting between lifetime and mean free path because of the inability to define an effective group velocity for all but the low frequency modes. This can be The additional disorder increases the fraction of localized states, but delocalized states still dominate. However, the diffusivity of the de-

localized states is diminished, weakening our faith in any literal interpretation of the minimum conductivity idea. ”<sup>50</sup>

Using the AF theory, In fact, for diffusons the diffusivity cannot be meaningfully represented as  $v^2 i / 3$  since  $v i$  and  $i$  cannot be independently defined.<sup>33</sup>

It is possible that the VC group velocities are an over-prediction for modes in a given interval of frequency, but is compensated for by an under-prediction of the lifetimes in the same interval of frequency when compared to the Gamma modes (Fig. ). The only constraint we have to compare against is the total vibrational conductivity, which shows good agreement when using the set of group velocities (Section ) and lifetimes (Section ) using VC-NMD. In this work, the Ioffe-Regel limit ( $\tau = 2\pi/\omega$ ) seems to be a lower limit for the mode lifetimes except for those predicted using VC-ALD (Fig. LJ-Gamma, LJ-Diff and SW-Diff ).

Particularly challenging is predicting a representative group velocity for modes in a disordered systems. Use of the VC approximation is a theoretically and computationally simple way to predict a representative group velocity.

As observed by Kittel, if the sound velocity is used instead of  $U$ ; and the interatomic spacing is used instead of the mean free path  $l$ ; then  $t_c(T)$  is qualitatively and semiquantitatively fit at temperatures above the plateau region. In fact, Slack showed that the same model is useful for crystalline insulators with strong scattering (waiting for ILL).?

Apparent- ly, naturally disordered systems like glasses tend to occur ‘va. We see no reason why this should occur, with  $D =$ , except for observing that the crossover between propaga- ting and localized states tends to be broad and gradual

While the models presented in, there is no theoretical justification for the lower limit to the the mode mean-free path.<sup>39</sup> For the lattices studied in this work, the more appropriate quantity to consider is the mode diffusivity since both the effective mode lifetime and group velocity are varying with frequency (Fig. ). Since the Allen-Feldman theory does not rely on the assumption of propagating phonons we expect the results for  $d$  to be valid even in the high-frequency regime, where the diffusivity cannot be factorized into a product of  $l(\omega)$  times a frequency-independent speed of sound.

For  $c = 0$  the group velocities are given from the dispersion (Section ).

In these ordered and disordered lattices, it is difficult to separate the contributions to the total vibrational conductivity from  $D_{ph}(\kappa)$  and  $D_{AF}$  unless the lower limit  $D_{CP,HS}$  or  $D_{AF,HS}$  are used.

While the expression for harmonic 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 conductivity reduction in dilute Ge-doped Si epitaxial layers is captured by mass perturbative disorder.<sup>13</sup> In this case,

the mass disorder is large ( $m_{Ge}/m_{Si} = 2.6$ ) but the overall disorder strength is dictated by the concentration. For example, as little as  $6.2 \times 10^{19} \text{ cm}^{-3}$  Ge ( $g = 3.1 \times 10^{-3}$ ) is enough to reduce the thermal conductivity of Si by almost a factor of 2.<sup>12</sup> In the case of the  $Ni_{0.55}Pd_{0.45}$  alloy, the atomic species are chemically similar but both the mass disorder ( $m_{Pd}/m_{Ni} \approx 2$ ) and concentration are large ( $g = 0.078$ ) and good agreement is seen with the Eq. .<sup>14</sup>

While , the effect of explicit disorder has been demonstrated in the calculation of the intrinsic phonon lifetimes.<sup>3</sup>

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.<sup>10</sup> 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.

The theory by Tamura is able to treat disorder scattering in an arbitrary crystal with dispersion. The theory, however, fails to predict the lifetimes of high-frequency modes, which are critical to the total thermal conductivity in LJ argon (see Fig. and ). To match the predicted phonon lifetime at high frequency for  $c = 0.05$  ( $\tau(\kappa) \propto \text{const.}$ , Fig. ), the Tamura theory requires a DOS which scales as  $D(\omega(\kappa)) \propto \text{const.}$ . Clearly from Fig. , this is not the case with either the VC or Gamma modes. To match the predicted phonon lifetime at high frequency for  $c = 0.5$  ( $\tau(\kappa) \propto 1/\omega(\kappa)$ , Fig. , also true for all  $c$  in SW silicon),

While Broido found that omission of optical scattering overpredicts the thermal conductivity of bulk Si by a factor of 2-3, optical modes contribute less than 5% to thermal conductivity itself. Similarly, the diffusivity adjusted thermal conductivities of SW Si are increased by less than 5%, demonstrating the unimportance of the high frequency “optical” modes in SW Si alloys.

the problem is with taud. VC-NMD agrees well with GK for both LJ and SW, while ALD-taud underpredicts for LJ. VC-NMD and ALD-taud use the same group velocity and classical specific heat.

High thermal conductivity materials tend to have a conductivity spectrum which is peaked in the low frequency range.(cite) It is in this range where the mode lifetimes follow closely the scalings with frequency which can be predicted by treating intrinsic and disorder scattering as perturbations (Eq. ).

In contrast, in LJ argon the high frequency phonon mode properties are critical to the thermal transport.(cite) While the low frequency phonon properties predicted by VC-NMD and VC-ALD agree, it is the failure of the perturbative models at high frequency which causes VC-ALD to underpredict. The failure to account

for harmonic disordered scattering due to the AF theory is responsible for causing both VC-NMD and VC-ALD to underpredict versus GK, which affects the high frequency modes significantly. LJ argon, with lower frequencies, lifetimes, and group velocities compared to “stiff” SW silicon, is considered a “soft” system. The predictions using VC-NMD, VC-ALD demonstrate the importance of explicit disorder modeling in “soft” systems and possible underprediction of the thermal properties.<sup>5</sup>

For SW silicon, the low frequency modes dominate thermal transport even in the heavily disordered alloy.(cite new Hopkins) It is thus unsurprising that predictions for SW silicon using VC-ALD agree well with VC-NMD and GK. This is also a plausible explanation for the success of predictions using VC-ALD and ab initio calculations compared to experiment for “stiff” systems (i.e. Si-Ge, GaN, and Diamond).(cite)

In SW silicon even the amorphous phase has significant contributions from propagating modes which can be considered to be phonons. This is can be seen by comparing the thermal conductivity predicted for the SW silicon amorphous phase ( $k_{GK} = 3 \text{ W/m-K}$  (cite)) compared to  $k_{CP,HS} = 0.5 \text{ W/m-K}$ . For LJ argon in the amorphous phase,  $k_{GK} = 0.121 \text{ W/m-K}$  and  $k_{CP,HS} = 0.12 \text{ W/m-K}$ , indicating that all important modes to thermal transport are non-propagating.

## V. SUMMARY

### Appendix A: Computational Cost

The key to incorporating the effects of disorder explicitly are the use of a large disordered supercells (Section ). However, the methods used in this work scale differently with the size of the supercell considered. The calculations in this work are trivially parallelizable except the MD simulations<sup>53</sup> and the eigenvalue solution of the Dynamical matrix (Section ).<sup>26</sup> Efficient MD codes scale linearly with the number of atoms in the system  $N_a$ , making the GK method an efficient method for predicting thermal conductivity. However, the computational cost of using large supercells for MD simulation, particularly because of the large number of time steps required (on the order of  $10^5 - 10^7$  depending on the system, time step used, etc (cite)), prohibit its use with typical ab initio methods such as plane-wave Density Functional Theory.(cite)

Using the VC-ALD method, the symmetries of the system can be used to drastically reduce the required computations.<sup>7,37,54,55</sup>

Compared to the calculation of the intrinsic phonon lifetimes, calculation of the defect lifetimes  $\tau_d(\kappa)$  (Eq. ) is negligible, which is the main reason for its use.(cite) Both VC-NMD and VC-ALD require the eigenvalue solution of a Dynamical matrix of size  $(3n, 3n)$  for each irreducible wavevector of the system size considered (Section ), which is negligible compared to the other caculations required for both of these methods.(cite)

For VC-ALD, the calculation of the intrinsic phonon lifetimes  $\tau_{p-p}(\kappa_\nu)$  scales as  $n^4$ ,<sup>37</sup> making calculations for large unit cells challenging.(cite)

The Gamma-NMD (Section ) and AF theory (Section ) require the eigenvalue solution of a large Dynamical matrix ( $3N_a, 3N_a$ ), the solution of which scales as  $(3N_a)^3$  (Section ). The AF theory is limited to small supercells using ab initio calculations, making it difficult to assess finite-size effects (Section ). For VC-NMD and Gamma-NMD, the MD simulation and large-matrix eigenvalue solution present real challenges when used with ab initio calculations.(cite)

Consider the following computational times for the methods used in this work for LJ argon and  $N_0 = 12$ . All calculations were performed on the same computing cluster and include the effect of using multiple processors (for example the VC-ALD calculations were run using 12 cpu for 4.1 hours):

AF = eigenvalue solution + thermal diffusivity calculation = 4.2 hours

VC-ALD time = 49.2 hours?

VC-NMD time = 102 hours for MD + 780 hours for NMD + negligible time to generate phonon frequencies and eigenvectors

LJ VC-Gamma = MD simulation + NMD + eigenvalue solution = 102 hours + 780 hours + 3.8 hours =

Parallel eigenvalue solvers exist for most ab initio packages, required to solve for the eigenvalues of the Hamiltonian matrix.(cite) Incorporating parallel eigenvalue solvers into existing Sparse eigenvalue solutions may be implemented for systems which are large enough and have short-range interactions.(cite)

## Appendix B: NMD using Non-Exact Normal Modes

The NMD method requires the atomic trajectories (positions and velocities) from an MD simulation. The MD simulations are performed using the package LAMMPS.<sup>53</sup> The lengths of the MD simulations were longer than 10 times the longest phonon lifetime in the system. These can be estimated a priori from the VC-ALD predicted phonon lifetimes. For LJ argon and SW silicon, the simulations were run for  $2^{20}$  and  $2^{22}$  time steps and the atomic trajectories were sampled every  $2^8$  and  $2^4$  time steps, respectively. Ensemble averaging was performed using 10 independent initial randomized velocity distributions.

For a normal mode which is a normal mode of the lattice supercell used for the MD simulations (Section ), the autocorrelation of the total and kinetic normal mode energy are damped exponentials with a decay time  $\tau(\kappa_\nu)$ , the kinetic energy autocorrelation with a sinusoidal oscillation frequency  $2\omega(\kappa_\nu)$ .(cite joe) When using the VC normal modes (Section ) to map the MD simulation trajectories for the explicitly disordered lattice supercells (Section ), the mode total and kinetic energy autocorrelation functions do not always follow simple functional

forms. This can be illustrated by using spectral-NMD in the frequency domain, where artifacts such as multiple peaks in an isolated mode's energy spectrum ( $\Phi$ ) can be observed (see Fig ).(cite) In the case of multiple peaks, the choice of which peak to fit to predict the phonon properties can be ambiguous. However, a lifetime can be predicted unambiguously using Eq. even with these multiple-peak artifacts, particularly because the autocorrelations are damped exponentially. This results is to be expected given that the atomic trajectories contain information about the lattice energy, which from general statistical physics principles will have exponential relaxation behavior in an equilibrium ensemble.<sup>56-58</sup>

These artifacts are not surprising given two considerations: 1) the MD simulations contain explicit disorder which influences the atomic trajectories 2) the VC normal modes are not the exact normal modes and of the explicitly disordered system. Discrepancies have been observed previously when the exact normal modes of the system are not used.(cite SED) However, the lifetimes predicted using VC-NMD are in fairly good agreement with those calculated using Gamma (Fig. ). Several studies have found good agreement for predictions of lifetimes and thermal conductivity using non-exact eigenvector mappings<sup>8,59</sup> in a wide-range of materials and phonon scattering conditions.<sup>6,8,59-61</sup> However, it is crucial that results using non-exact mappings are compared to as many alternative methods as possible. In this work, VC-NMD is compared to the other methods Gamma (Section ), GK (Section ), and VC-ALD (Section ). It is important to remember that the VC normal modes are exact in the limit  $c \rightarrow 0$ . Use of the VC modes at large  $c$  pushes the limits of the approximation, but is useful for predicting an effective group velocity (Section ) and the predicted lifetimes agree well with those using Gamma (Section ).

## Appendix C: Calculation of the Gamma Mode Structure Factors

To calculate  $S^{L,T}(\omega)$  for a finite-size system, the delta function in Eq. (??) is broadened using a Lorentzian function with a full-width at half maximum  $\Gamma_{FMHW} = \delta_{\omega,avg}$ , where  $\delta_{\omega,avg}$  is the average frequency spacing. Allen et al<sup>35</sup> demonstrated using a model of a-Si that the structure factor for large wavevector broadens so that the linewidth  $\Gamma_{SF} > \omega$ .<sup>38</sup> For the system sizes studied,  $\Gamma_{SF}$  scale with the broadening factor  $\Gamma_{FMHW}$  for all peaks except those at high frequencies.

For the range of broadening factors considered ( $\Gamma_{FMHW} = \delta_{\omega,avg}$  to  $50\delta_{\omega,avg}$ ) the linewidths extracted for all  $c$  generally satisfy  $\Gamma_{SF} > \omega$ . For all broadening factors, the linewidths (inverse lifetimes,  $\tau_{SF} = 1/2\Gamma_{SF}$ ) at high frequency are in better agreement with the lifetimes predicted by VC-NMD rather than VC-ALD, where generally  $\tau > 2\pi/\omega$  (Ioffe-Refel limit, Fig. ).<sup>38</sup> This gives a bit more justification for the use of the VC

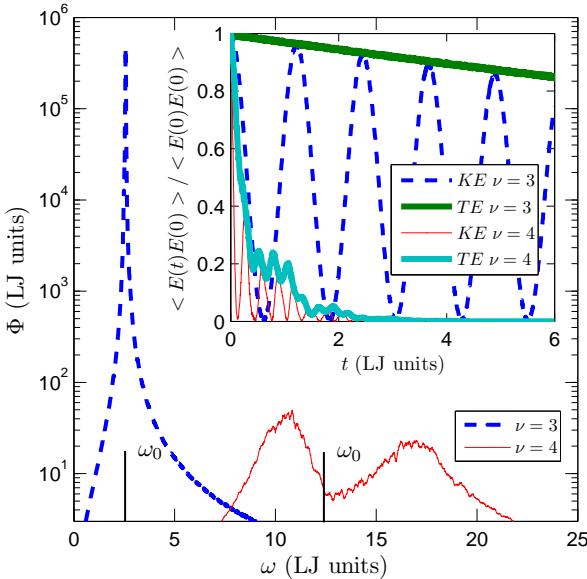


FIG. 10: The spectral energy density  $\Phi$  of two modes (polarizations  $\nu = 3, 4$  at wavevector  $[0.2 \ 0 \ 0]$ ) calculated using VC-NMD for a mass disordered LJ FCC supercell ( $N_0 = 8$  and  $c = 0.5$ , Section ). The VC dispersion-predicted peaks are labeled by  $\omega_0$ . Inset: the same mode's energy (kinetic (KE) and total (TE)) autocorrelation functions. Note the additional harmonic effects in the KE and TE autocorelation functions for  $\nu = 4$  which are due to the double peaks in  $\Phi$ . A mode lifetime can be extracted unambiguously using the integral of the TE autocorrelation function (Section ).

predicted group velocities both VC-NMD and VC-ALD, even for large wavevector and  $c$ .

In general, the polarization of the eigenvectors  $e_{\nu}^{(\kappa b)}$  will not be purely transverse or longitudinal along the reciprocal directions. Even for the simple LJ argon system, this can make it difficult to uniquely identify then different polarizations with the various peaks in the structure factors. For SW silicon, similar good agreement can be seen along the high symmetry directions for the acoustic branches, while the optical modes and more complicated polarizations are too difficult to identify in an automated way. In general, the acoustic branches can be identified, provided they are well separated in energy (or frequency) from any optical branches.<sup>33,59</sup>

#### Appendix D: Finite Simulation-Size Scaling for Thermal Conductivity

To predict a bulk thermal conductivity, extrapolation is used by the following finite size scaling  $1/k \propto 1/N_0$ . For VC-NMD and VC-ALD, the validity of the finite-size scaling requires the low frequency modes in the finite system to be dominated by intrinsic scattering ( $\tau(\kappa) \propto \omega(\kappa)^{-2}$ , Section ) and follow the Debye approximation with respect to  $v_{g,n}$  (Section ) and DOS  $D(\omega(\kappa))$

(Section ).<sup>6,7</sup> For LJ argon, this requirement is satisfied for modest system sizes (for  $N_0 = 6$  to 12) so that both VC-NMD and VC-ALD predictions can be extrapolated to a bulk value. For SW silicon, the thermal conductivity is dominated by low-frequency modes (Fig. ). Because of this, large system sizes (up to  $N_0 = 24$ ) are needed to satisfy the extrapolation requirements and only VC-ALD can be used.(cite) This underlines the computational efficiency of the VC-ALD method which is necessary when computationally expensive ab initio methods are used (Section ).<sup>2,3,5,7</sup> For the GK method, the finite size extrapolation is used for both LJ argon and SW silicon for smaller system sizes  $N_0 \leq 12$ . The validity of this result can be explained in terms of a combination of effects which are specific to the MD simulations.<sup>7</sup> In fact, for  $c = 0$  the GK results are independent of system size for  $N_0 = 4$  to  $N_0 = 12$  for both LJ argon and SW silicon.

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