

# 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*

(Dated: November 25, 2012)

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 theory using ab initio calculations. However, computational costs limit the size of unit cells in ab initio calculations to be less than 100 atoms, making it difficult to directly incorporate the effects of disorder. Alternatively, theory that treats disorder as a harmonic perturbation can be used to estimate the reduction in phonon lifetimes due to disorder scattering without the use of a large unit cell. 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). 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. 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.

## I. INTRODUCTION

For thermoelectric device applications, minimizing a thermoelectric material's thermal conductivity has become a promising technique for increasing  $ZT > 3$ .<sup>1,2</sup> In semiconductor alloys, understanding the effect of disorder is necessary for optimizing ZT by further lowering thermal conductivity.<sup>3-6</sup>

Abeles first introduced the idea of using a virtual crystal (VC) to replace a disordered one by treating both disorder and anharmonicity as perturbations.<sup>7</sup>

Many experimental results and trends in thermal conductivity of a range of materials can be explained using the VC approximation. However, a complete description of the thermal transport in alloys requires modeling intrinsic and disordered scattering to predict phonon lifetimes.

Modeling phonon lifetimes is usually done by treating both intrinsic and disordered scattering as perturbations under the VC approximation. The relative simplicity of this approach allows the use of computationally expensive ab-initio methods. Recently, work using ab-initio calculations, anharmonic lattice dynamics (ALD) and the VC approximation to predict phonon mode frequencies, lifetimes and group velocities of materials with relatively large<sup>8,9</sup> moderate<sup>7</sup>, and small<sup>6</sup> thermal conductivities. However, no comprehensive study has been performed to assess the applicability of this perturbative approach for a range of heavily disordered systems using multiple predictive methods.

The goal of this work is to verify the use of the virtual crystal approximation for predicting thermal con-

ductivity by a detailed comparison of 3 predictive methods: MD-based normal mode decomposition (NMD) and green-kubo (GK), and anharmonic lattice dynamics (ALD) which treats the harmonic and anharmonic phonon scattering as perturbations. When used with the VC approximation, these methods are referred to as VC-NMD and VC-ALD. Two model alloy systems with mass defects ( $m_{1-c}^a m_c^b$ ) 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, spanning range of perturbative to heavy disorder. These two alloyed systems have very different ranges of phonon frequencies, lifetimes, group velocities and total thermal conductivity. For Stillinger-Weber silicon, VC-ALD predicts phonon properties and thermal VC-NMD and GK. For Lennard-Jones argon, the VC-ALD approximation underpredicts the high frequency phonon lifetimes, leading to an underpredicting of its thermal conductivity. The different thermal conductivity spectra of the modeled and the breakdown of the perturbative scattering models are examined.

## II. VIRTUAL CRYSTAL (VC) APPROXIMATION

Abeles introduced the idea of using a virtual (perfect) crystal to replace a disordered one, computing the thermal conductivity of Si/Ge alloys by treating both disorder and anharmonicity as perturbations.<sup>7</sup> We calculate at all compositions of mass variation ( $m_{1-c}^a m_c^b$ ) the phonon modes of the virtual crystal (which has a temperature de-

pendent lattice parameter, mass, and force constants of that particular composition) and derive from the frequencies (Section ), group velocities (Section ), and lifetimes (Section ) to calculate thermal conductivity (Section ).

Many experimental results and trends in thermal conductivity of a range of materials can be explained using the VC approximation.

Based on lattice dynamics calculations, the sound speed in simple alloys follows a simple scaling with mass or bulk modulus (spring constant) of the virtual crystal (see Section ). This is one explanation for the decreased thermal conductivity of germanium versus silicon. However, a complete description of the thermal transport in alloys requires modeling intrinsic and disordered scattering (lifetimes) of phonons.

Cahill shows that conductivity of dilute Ge-doped Si epitaxial layers agrees with a virtual crystal approximation with a phonon lifetime term that treats the defects as a perturbation (see section).<sup>10</sup> Garg used ab initio calculations with anharmonic lattice dynamics (ALD) and the virtual crystal approximation (referred to as VC-ALD) to predict the thermal conductivity of Si-Ge alloys for all concentrations, obtaining good agreement with experiment.<sup>8</sup> A detailed study of PbTe/PbSe systems demonstrate the importance of bond environment for alloys.<sup>6</sup>

The computational studies discussed above were limited to the use of VC-ALD because of the computational cost of ab initio calculations. Using empirical potentials, we study the effects of explicit disorder in the following sections.

### A. Kinetic Theory

For a perfect system, all vibrational modes are phonons.

Using the single-mode relaxation time approximation<sup>11</sup> as an approximate solution of the Boltzmann transport equation<sup>12</sup> gives

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

Here,  $c_{ph}$  is the phonon volumetric specific heat and  $v_{g,\mathbf{n}}$  is the component of the group velocity vector in direction  $\mathbf{n}$ . Since the systems we consider are classical and obey Maxwell-Boltzmann statistics,<sup>13</sup> the specific heat is  $k_B/V$  per mode in the harmonic limit where  $V$  is the system volume. This approximation is used for all calculations in this work so that direct comparisons can be made for all predictions.

Each mode contributing to the thermal conductivity has a frequency  $\omega(\boldsymbol{\kappa})$ , which is related to the energy of a phonon in this mode by  $\hbar\omega(\boldsymbol{\kappa})$ . In a perfect system, the allowed energies (frequencies) are eigenvalues of the system's dynamical matrix,  $D(\boldsymbol{\kappa})$ , which relates the mode

eigenvector ( $e(\boldsymbol{\kappa}_\alpha^b)$ ) and eigenvalue by

$$D(\boldsymbol{\kappa}) e(\boldsymbol{\kappa}_\alpha^b) = \omega(\boldsymbol{\kappa})^2 e(\boldsymbol{\kappa}_\alpha^b). \quad (2)$$

In a crystal all vibrational modes are plane-waves and as such can be identified by a unique wave-vector  $\boldsymbol{\kappa}$ , eigenvector  $e(\boldsymbol{\kappa}_\alpha^b)$ , and a possibly degenerate frequency  $\omega(\boldsymbol{\kappa})$ . In a disordered structure, such as a crystal lattice with randomly arranged and differing mass species, all vibrational modes exist at the wavevector [000]. In general, these disordered vibrational modes will not be pure plane-waves and will be non-degenerate in frequency. We examine

It thus becomes difficult to predict an effective dispersion

### B. Phonon Group Velocities

The group velocity vector is the gradient of the dispersion curves (i.e.,  $\partial\omega/\partial\boldsymbol{\kappa}$ ), which can be calculated from the frequencies and wavevectors using finite differences. In this work, the group velocities are calculated using finite difference and quasi-harmonic lattice dynamics because a very small finite difference can be used which reduces the error.<sup>?</sup>

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

$$\Lambda(\boldsymbol{\kappa}) = |\mathbf{v}_g| \tau(\boldsymbol{\kappa}), \quad (3)$$

which requires a group velocity.

In ordered systems, the group velocity generally scales with both the density and stiffness of the material. For example, the reduced vibrational conductivity of Ge compared to Si can be (partially) explained in both terms of the  $\bar{m}$  (germanium has a larger density  $\rho$  than silicon) and the group velocity (germanium has a smaller bulk modulus  $B$ , and  $v_g \propto \sqrt{B/\rho}$ ). Thus, for alloys, there should also be a corresponding scaling of the group velocity with the alloy's concentration (mass density).

### C. VC and Gamma DOS Comparison

The low frequency

Similar agreement at low frequencies was found in ab initio predictions for  $Si_cGe_{1-c}$ .<sup>8</sup> Bouchard show that alloy DOS at low frequency varies smoothly with concentration for a- $Si_cGe_{1-c}$ .<sup>14</sup>

The frequencies of the Gamme point modes are shifted slightly higher because of the explicit use of atoms of lighter mass than the virtual mass.

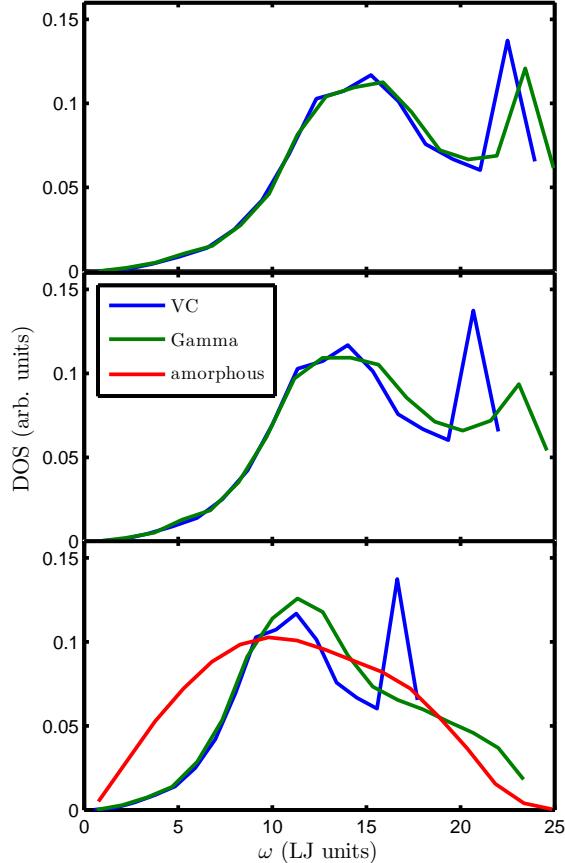


FIG. 1: virtual crystal results

#### D. Structure Factor of Gamma Point Modes

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

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

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

Demonstrates the importance of dispersion, even along different lattice directions ([100] vs [111]) and polarizations ( $S^L, T$ ).

With increasing concentration, the structure factor spreads in width, particularly at high frequencies. The VC mass becomes larger and the peaks in the structure factor shift to lower frequencies. The peaks in the structure factor for Gamma point modes are shifted to slightly higher frequencies because of the explicit use of masses

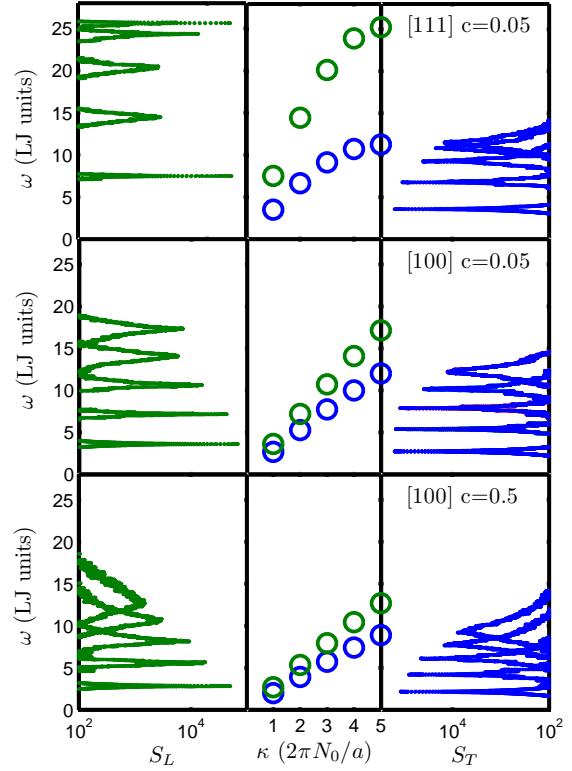


FIG. 2: virtual crystal results

less than the VC mass, and effect which can also be seen in the DOS comparisons (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. ). These well-defined peaks at all wavevectors is unique to the disordered lattice. Typically, the structure factor for amorphous materials have well-defined peaks only for small wavevector.(cite) The frequencies extracted from the structure factors agree with the VC predictions to less than 5% at the highest frequencies. Because of this, we use the group velocities predicted by the VC dispersion in both our VC-NMD and VC-ALD calculations for consistency.

Duda shows the reduction in group velocity of moderate to high frequency modes in a 1D alloy are drastically reduced by considering the effects of zone folding.<sup>15</sup> Based on the structure factors in Fig. , the reduction due to zone folding seems to underpredict the group velocity of moderate to high frequency modes.

#### E. Phonon Lifetimes

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

where  $\tau_{p-p}(\kappa_\nu)$  accounts for phonon-phonon scattering,  $\tau_b(\kappa_\nu)$  accounts for boundary scattering,  $\tau_d(\kappa_\nu)$  accounts for defect scattering.

Phonon-phonon scattering ( $\tau_{p-p}(\kappa_\nu)$ ) is typically treated using anharmonic perturbation theory including only 3-phonon processes.<sup>6,8,16</sup> It has been estimated that the effects of higher order phonon processes are small<sup>17</sup>. At low frequencies,  $\tau_{p-p}(\kappa_\nu)$  follows a scaling due to both normal ( $B_1\omega^2$ ) and umklapp ( $B_2\omega^2$ ) 3-phonon scattering processes, where the density of states is Debye-like. The constants  $B_1$  and  $B_2$  are typically fit to experimental data.

Using harmonic perturbation theory, Tamura gives a general expression for mass point defect scattering<sup>18</sup>

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

where  $g(b) = \sum_i c_i(b)(1 - m_i(b)/\bar{m}(b))^2$ ,  $N$  is the number of unit cells. and  $c_i$  is the fraction,  $m_i$  is the mass, and  $\bar{m}_i$  is the average mass of the i-th species.

For the simple single species systems considered in this work,  $\frac{1}{\tau_d(\kappa_\nu)} = \frac{\pi}{2} g \omega(\kappa_\nu)^2 D(\omega(\kappa_\nu))$ , where  $D(\omega(\kappa_\nu))$  is the density of states. Under the Debye-approximation, 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 where the Debye approximation is valid.

Bond disorder can be accounted for using a similar expression with an average atomic radius or suitable scattering cross-section.<sup>19,20</sup> The effect of bond and mass disorder has been investigated computationally by Skye and Schelling for Si/Ge<sup>21</sup>, where it was shown that mass disorder is the dominant scattering mechanism. In this work we consider only mass disorder.

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>22</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  $6.2 \times 10^{19} cm^{-3}$  Ge ( $g = 3.1 \times 10^{-3}$ ) is enough to reduce the thermal conductivity of Si by almost a factor of 2.<sup>10</sup> Even 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>23</sup>

Computational results for moderate to high thermal conductivity alloys show good to excellent agreement with experimental results<sup>8,9</sup>. Computational results for

small thermal conductivity alloys show universal trends but little experimental results are available for comparison.

## F. Phonon Lifetime Predictions

### 1. Normal Mode Decomposition (NMD)

As an alternative to VC-ALD models for predicting phonon lifetimes, we also use the normal mode decomposition (NMD) method. NMD maps the atomic coordinates (position and velocities) of all atoms in an MD simulation onto vibrational normal modes.(cite) The vibrational mode frequencies ( $\omega(\kappa_\nu)$ ) and eigenvectors ( $e(\kappa_\nu \alpha^b)$ ) are necessary for the mapping. The vibrational normal mode coordinates,  $q(\kappa_\nu; t)$  and  $dot{q}(\kappa_\nu; t)$ , are required to calculate the total vibrational normal mode energy  $E(\kappa_\nu)(t)$ .

The phonon lifetime is predicted using

$$\tau(\kappa_\nu) = \int_0^\infty \frac{\langle E(\kappa_\nu; t) E(\kappa_\nu; 0) \rangle}{\langle E(\kappa_\nu; 0) E(\kappa_\nu; 0) \rangle} dt. \quad (9)$$

This is necessary for the disordered systems where spectral NMD can produce multiple peaks in an isolated mode's power spectrum. This feature is not surprising given two considerations: 1) the MD simulations contain explicit disorder which influences the atomic trajectories 2) the normal modes are mapped without using the exact eigenvectors and frequencies of the explicitly disordered system (see Fig. and ).

Under the VC approximation, the phonon eigenvectors are those of pure plane-waves by definition. In a disordered supercell, the vibrational modes are not pure plane-waves (phonons) (see Section) and exist at the Gamma point ([000]). Lifetimes NMD and Gamma-NMD, are examined in Section and referred

## G. VC-NMD and Gamma Point Phonon Lifetimes

Gamma refers to mapping using the eigenvectors of the exact harmonic eigenmodes of the disordered supercell.

For VC-NMD, the normal mode mappings are performed using eigenvectors which are plane waves.

eigenvector mappings<sup>24,25</sup> use NMD to predict the phonon properties of PbTe using a classical model.<sup>26</sup> half-huesler uses  $\Phi'$  and ALD, find good agreement.<sup>27</sup> finds increased scattering in water-filled CNTs.<sup>28</sup> finds increased scattering of phonons in CNTs on a substrate.

In these studies, the atomic coordinates are being mapped onto modes which are not eigenmodes of the system's Hamiltonian. Still, the spectral widths (inverse lifetimes) of these mappings contain information about the scattering time scales associated with these modes.

Previous studies have used the spectral NMD using exact and non-exact mode eigenvectors to extract mode

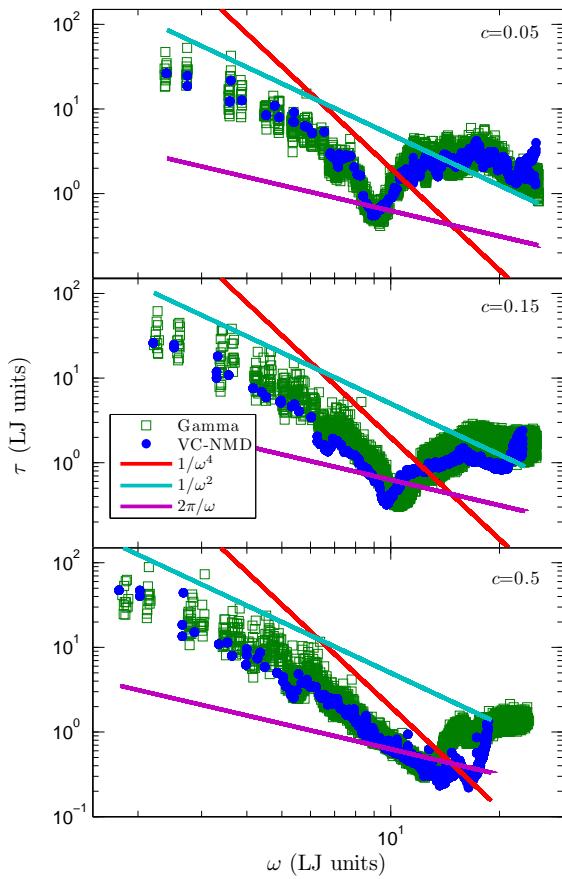


FIG. 3: virtual crystal results

timescales.(cite) The lifetimes using these mappings contain the effects of both intrinsic(cite) and disorder scattering(cite). Interpretation of these timescales as phonon lifetimes has led to succesful thermal conductivity predictions in a range of ordered and disordered materials. (cite) Given the possible ambiguity of the lifetimes predicted using VC-NMD, it is necessary to compare the predicted thermal conductivities using a range of methods which posses no such ambiguity (such as VC-ALD and GK, see Section ).

## H. Vibrational Mode Diffusivity

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

$$D_{ph}(\omega(\kappa)) = \mathbf{v}_{g,\mathbf{n}}^2(\kappa) \tau(\kappa). \quad (10)$$

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.(cite) With sufficient disorder, the harmonic AF

theory is capable of accurately predicting a finite thermal conductivity.(cite shenogin, FKAW) In the classical limit, the AF thermal conductivity is written as

$$k_{AF} = \sum_{\omega} \frac{k_B}{V} D_{AF}(\omega), \quad (11)$$

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

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

$$D_{AF,HS} = \frac{1}{3} v_s a. \quad (12)$$

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

$$D_{CP,HS} = 0.403 v_s a. \quad (13)$$

The CP thermal conductivity prediction in the HS limit is

$$k_{CP,HS} = \left(\frac{\pi}{6}\right)^{1/3} \left(\frac{3}{2}\right) \frac{k_B}{V_b} b v_s a, \quad (14)$$

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>29</sup> Comparing with Eq., the AF,HS limit predicts a mode diffusivity and thermal conductivity which is %20 smaller then CP,HS.<sup>29</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  $\tau = 1/\omega$  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. Finite system size frequency spacings limit the  $D_{AF}$  of the lowest frequency modes using the harmonic AF theory. In the infinite-size, low-frequency limit the AF conductivity of a disordered lattice is divergent due to lack of anharmonic phonon-phonon scattering.(cite) While the low frequency modes are not treated properly in the harmonic AF theory,  $D_{AF}$  of high frequency modes in the heavily disordered ( $c = 0.5$ ) LJ alloy approaches that of similar frequency modes in the amorphous phase (Fig. ). 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  $k_{AF} = 0.099 W/m = K$  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. In fact, thes

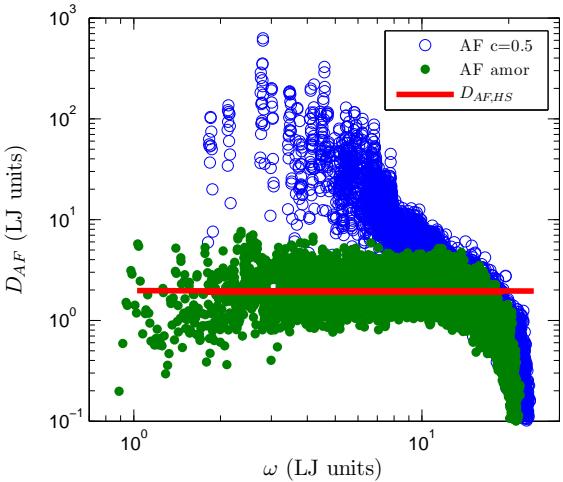


FIG. 4: gamma point results

### I. VC-NMD and VC-ALD Mode Diffusivities

We now compare the phonon mode diffusivities,  $D_{ph}(\omega_\nu^\kappa)$  predicted by both VC-NMD and VC-ALD to the proposed lower limit  $D_{AF,HS} = (1/3)v_s a$ . 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.

For the VC-ALD method, the intrinsic  $\tau_\nu^\kappa$  is calculated using the method described in.<sup>16</sup> To calculate the disordered lifetimes (Eq. ), it is necessary to broaden the  $\delta$  function using a Lorentzian function. For all calculations, the Lorentzian was broadened using a value of 100 times the mean level spacing. The results do not differ significantly if this broadening value is varied by changing it manually or making the system size ( $N_0$ ) bigger.

For LJ argon, VC-NMD predicts lifetimes which are generally larger than the period  $(2\pi/\omega_\nu^\kappa)$  of the vibrational oscillation (Ioffe-Regel limit)(cite), and actually increase with increasing frequency for small intervals (Fig. ). 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  $c_{ph}(\kappa)$  and  $v_g(\kappa)$ , 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. ) compared to VC-NMD.

For both VC-NMD and VC-ALD, a significant number of modes have  $D_{ph}(l; t) D_{AF,HS}$ . 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  $D_{ph}(l; t) D_{AF,HS}$  is given  $D_{ph} = D_{AF,HS}$ . The results of this adjustment are

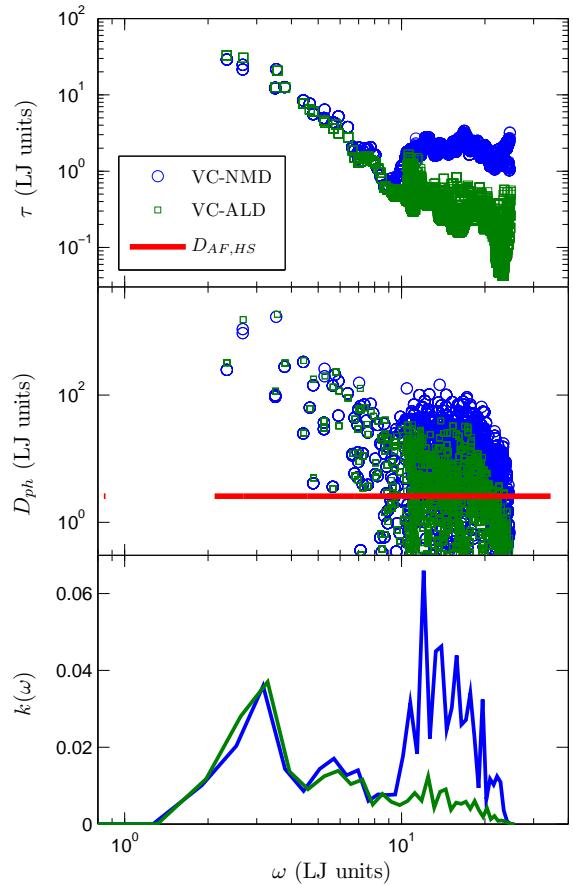


FIG. 5: gamma point results

examined in the next 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>30</sup>

In fact, the beginning breakdown of the intrinsic scattering model  $(\tau_{p-p}(\kappa))$  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>16</sup>

For LJ argon, bulk thermal conductivity predictions

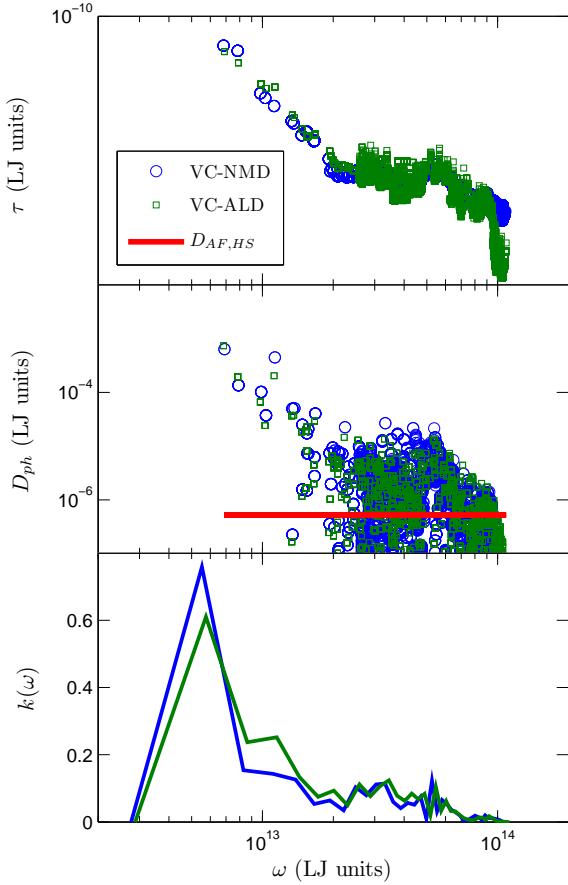


FIG. 6: gamma point results

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

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>7</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

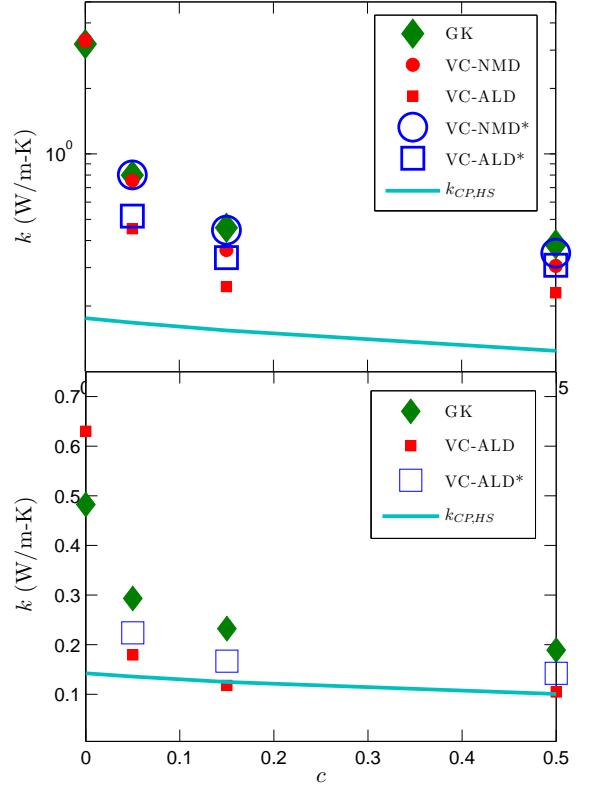


FIG. 7: The vibrational conductivity of LJ alloys predicted using MD simulations and the Green-Kubo method. The predicted thermal conductivities are for a LJ alloy of the form  $m_a^a - cm_c^b$ , where  $m^a = 1$ ,  $m^b = 3$ , and  $m_r = m^a/m^b = 3$  (in LJ units). As the alloy concentration is increased 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.

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),

VC-NMD and VC-ALD underpredict vs GK by about 20-30, while for LJ the underprediction is 2-300

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.

#### IV. DISCUSSION

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.

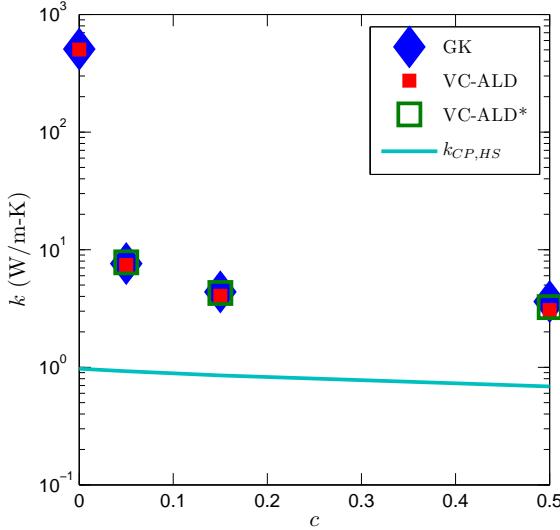


FIG. 8: The vibrational conductivity of LJ alloys predicted using MD simulations and the Green-Kubo method. The predicted thermal conductivities are for a LJ alloy of the form  $m_1^a m_c^b$ , where  $m^a = 1$ ,  $m^b = 3$ , and  $m_r = m^a/m^b = 3$  (in LJ units). As the alloy concentration is increased 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.

For diffusons, one can still assign a mfp by the following:

Particularly challenging is predicting a representative group velocity for modes in a disordered systems. Predicting a representative group velocity for modes in a disordered system is perhaps more important (and challenging) than predicting mode lifetimes. Use of the VC approximation is a theoretically and computationally simple way to predict a representative group velocity.

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>6</sup>

For SW silicon, the low frequency modes dominate thermal transport even in the heavily disordered alloy. 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 of using VC-ALD and ab initio calculations compared to experiment for “stiff” systems Si-Ge, GaN, and Diamond.(cite) (cite new Hopkins)

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 ( $k_{GK} = 2$  W/m-K) compared to  $k_{CP,HS} = 0.5$  W/m-K. For LJ argon in the amorphous phase,  $k_{GK} = 0.121$  W/m-K and  $k_{CP,HS} = 0.12$  W/m-K, indicating that all important modes to thermal transport are non-propagating.

### A. Boundary Scattering

Boundary scattering is responsible for decreasing the long lifetimes (mean free paths) of low frequency phonons which carry a significant amount of heat, making it particularly effective at decreasing the thermal conductivity of systems with length scale of 100s of nm and less.<sup>31</sup>

First-principles calculations on some thermoelectric materials show that phonons have a wide MFP distribution, and hence relatively large nanostructures can reduce their lattice thermal conductivity.<sup>5,18,19</sup> On the other hand, recent first-principles calculations have shown that the distribution is much narrower for PbTe,<sup>20</sup> and thus, further characterizations of the distributions and the associated detailed heat conduction of lead chalcogenides are important for better material design.

## V. SUMMARY

### Appendix A: Allowed Wavevectors in Ordered and Disordered Systems

The phonon spectral energy is defined for the allowed wavevectors of a crystal, which can be specified from the crystal structure’s Bravais lattice and its basis, i.e. unit cell. A  $D$ -dimensional Bravais lattice is a collection of points with positions

$$\mathbf{u}_0(l) = \sum_{\alpha}^{D} N_{\alpha} \mathbf{a}_{\alpha} \quad (\text{A1})$$

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

the crystal can be described by

$$\mathbf{u}_0(l) = \mathbf{u}_0(0) + \mathbf{u}_0(b) \quad (\text{A2})$$

where  $\mathbf{u}_0(l)$  is the equilibrium position of the  $l^{\text{th}}$  unit cell and  $\mathbf{u}_0(b)$  is the equilibrium position of the  $b^{\text{th}}$  atom in the unit cell relative to  $\mathbf{u}_0(0)$ . For the LJ systems studied here, the cubic conventional cells are used with four atoms per unit cell.<sup>7</sup> For our MD simulations, cubic simulation domains with periodic boundary conditions are used with  $N_1 = N_2 = N_3 = N_0$ .<sup>7</sup><sup>8</sup> The allowed wavevectors for such crystal structures are

$$\kappa = \sum_{\alpha} \mathbf{b}_{\alpha} \frac{n_{\alpha}}{N_{\alpha}}, \quad (\text{A3})$$

where  $\mathbf{b}_{\alpha}$  are the reciprocal lattice vectors<sup>7</sup> and  $-N_{\alpha}/2 < n_{\alpha} \leq N_{\alpha}/2$ , where  $n_{\alpha}$  are integers and  $N_{\alpha}$  are even integers.<sup>7</sup> The wavevectors are taken to be in the first Brioullin zone.<sup>7</sup>

Strictly speaking, the only allowed wavevector in a disordered system is the gamma point ( $\kappa = [000]$ ). As such, the lattice dynamics calculations are performed at the gamma point:

### 1. Normal Mode Decomposition

If  $\gamma(\nu) > \omega(\nu)$ , then the vibrational mode is over-damped. Discuss why real-space method is necessary in this case.

### Appendix B: 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 criteria for the validity of this finite size scaling is the low frequency modes in the finite system must be dominated by intrinsic scattering such that  $\tau(\nu) \propto \omega(\nu)^{-2}$  and approximately follow the Debye approximation with respect to  $v_{g,n}$  and DOS  $D(\omega(\nu))$ .<sup>(cite)</sup> For LJ argon, this requirement is satisfied for modest system sizes (up to  $N_0 = 10$ ) 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. Because of this, large system sizes (up to  $N_0 = 24$ ) are needed to satisfy the extrapolation requirement and only VC-ALD can be used.<sup>(cite)</sup> This underlines the computational efficiency of the VC-ALD method which is necessary when computationally expensive ab initio methods are used.<sup>(cite)</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>32</sup>

