

Evaluation of the Virtual Crystal Approximation for Predicting Thermal Conductivity

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(Dated: November 24, 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 $ZT > 3$.^{1,2} In semiconductor alloys, understanding the effect of disorder is necessary for optimizing ZT by further lowering thermal conductivity.³⁻⁶

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

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 transpot in alloys requires modeling intrinsic and disordered scattering (lifetimes) of phonons.

Modeling phonon lifetimes is usually done by treating both intrinsic and disordered scattering as pertubations under the VC approximation. The relative simplicitiy of this approach allows the use of compuatioanlly expensive ab-initio methods. Recently, work using ab-initio calculations and the VC approximation to predict phonon mode frequencies, lifetimes and group velocities of materials with realltively large^{8?} moderate⁷, and small⁶ thermal conductivities. However, no comprehensive study has

been performed to asses the applicability of this perturbative approach for a range of heavily disorered systems using multiple predictive methods.

The goal of this work is to verify the use of the virtual crystal approximation for predicting thermal conductivity 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. 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. These two alloyed systems have different ranges of phonon frequencies, lifetimes, and mean free paths. For Stillinger-Weber silicon, ALD predicts phonon properties and thermal conductivity in good agreement with MD-based methods NMD and GK. For Lennard-Jones argon, the VC approximation underpredicts the high frequency phonon lifetimes, leading to an underpredicting of its thermal conductivity. Vibrational mode properites of

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.⁷ 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 dependent 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).

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).⁹ 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.⁸ A detailed study of PbTe/PbSe systems demonstrate the importance of bond environment for alloys.⁶

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 approximation¹⁰ as an approximate solution of the Boltzmann transport equation¹¹ 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 $\mathbf{v}_{g,\mathbf{n}}$ is the component of the group velocity vector in direction \mathbf{n} . Since the systems we consider are classical and obey Maxwell-Boltzmann statistics,¹² 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.⁷

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 in terms of the \bar{m} (germanium has a larger density ρ 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} .⁸ Bouchard show that alloy DOS at low frequency varies smoothly with concentration for a- Si_cGe_{1-c} .¹⁵

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

D. Structure Factor of Gamma Point Modes

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

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

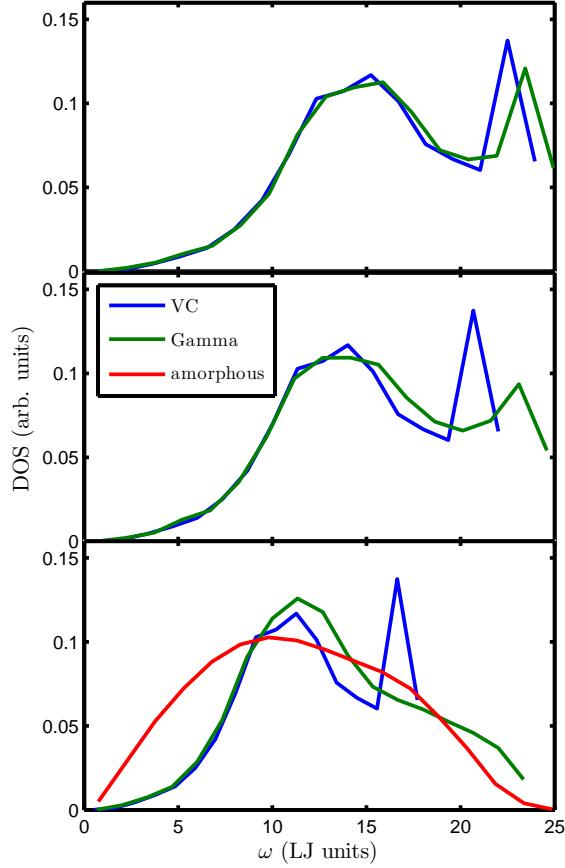


FIG. 1: virtual crystal results

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

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 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 detected. The frequencies extracted from the structure factors agree with the VC predictions to within less than 5%. From the dispersion, the mode group velocities can be predicted (see Section), which is necessary to predict thermal conductivity (see Section). The VC predicted group velocities are used

Duda shows the reduction in group velocity of disordered systems.¹⁶

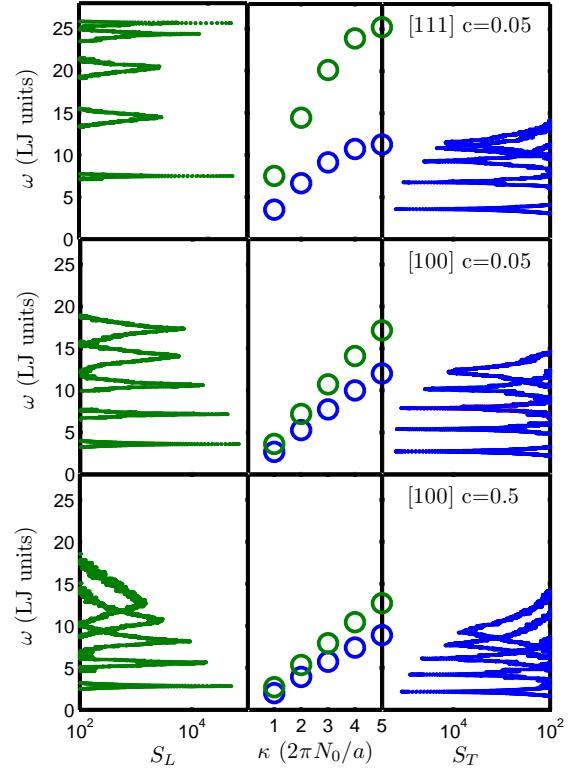


FIG. 2: virtual crystal results

E. Phonon Lifetimes

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

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

Phonon-phonon scattering ($\tau_{p-p}(\nu)$) is typically treated using anharmonic perturbation theory including only 3-phonon processes.^{6,8,17} It has been estimated that the effects of higher order phonon processes are small¹⁸. At low frequencies, $\tau_{p-p}(\nu)$ 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 scattering¹⁹

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

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, $\frac{1}{\tau_d(\kappa)} = \frac{\pi}{2} g \omega(\kappa)^2 D(\omega(\kappa))$, where $D(\omega(\kappa))$ 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 (ω^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.^{20,21} The effect of bond and mass disorder has been investigated computationally by Skye and Schelling for Si/Ge²², 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.²³ 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 2.⁹ 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.²⁴

Computational results for moderate to high thermal conductivity alloys show good to excellent agreement with experimental results^{8? ?}. 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)

We use the normal mode decomposition (NMD) method

The phonon lifetime is predicted using the following

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

The vibrational normal mode coordinate, $q(\kappa; t)$ and $qdot(\kappa; t)$, is required to calculate the vibrational normal mode energy $E(\kappa)(t)$. The phonon mode eigenvectors, $e(\kappa)_\alpha$, are required to map the

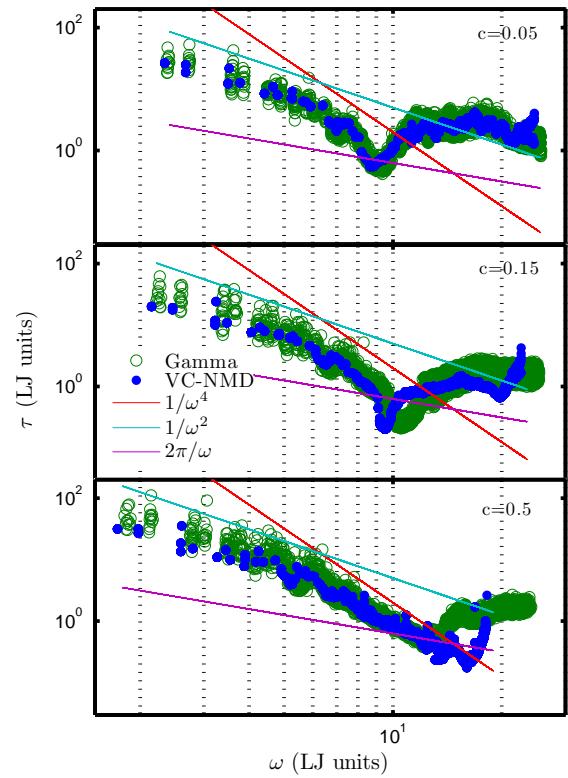


FIG. 3: virtual crystal results

atomic coordinates onto the phonon normal modes. Under the VC approximation, the phonon eigenvectors are those of pure plane-waves. In a disordered supercell, the vibrational modes are not purely plane-wave (phonon) (see Section) and exist at the Gamma point ([000]). Both cases are compared in the next section.

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

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^{25,26} use NMD to predict the phonon properties of PbTe using a classical model.²⁷ half-huesler uses Φ' and ALD, find good agreement.²⁸ finds increased scattering in water-filled CNTs.²⁹ 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.

H. Mode Diffusivity

The high scatter limit is given as:

$$k_{CP,HS} = \left(\frac{\pi}{6}\right)^{1/3} \left(\frac{3}{2}\right) \frac{k_B}{V_b} b v_s a \quad (10)$$

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).³⁰ The characteristic diffusivity of each mode in the high-scatter limit is

$$D_{CP,HS} = 0.403 v_s a. \quad (11)$$

where the vibrational mode MFP is taken to be a .

From the disordered harmonic theory of Allen-Feldman (referred to as AF), the thermal conductivity in the high-scatter limit can be written as

$$k_{AF,HS} = \sum_i^{modes} \frac{k_B}{V} D_{AF,HS} \quad (12)$$

where the characteristic diffusivity of each mode in the high-scatter limit is

$$D_{AF,HS} = \frac{1}{3} v_s a. \quad (13)$$

Comparing with Eq., the AF HS limit predicts a mode diffusivity and thermal conductivity which is %20 smaller.³⁰

$$k_{AF} = 0.14 W/m - K \quad k_{AF} = 0.36 W/m - K$$

Broido found that omission of optical scattering over-predicts thermal conductivity by a factor of 2-3, optical modes contribute less than 5% to thermal conductivity itself. The diffusivity adjusted thermal conductivities are increased by less than 5%,

I. VC-NMD and VC-ALD Mode Diffusivities

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.³¹

The thermal conductivity of amorphous solids at low temperatures contain quantum statistical effects.³²

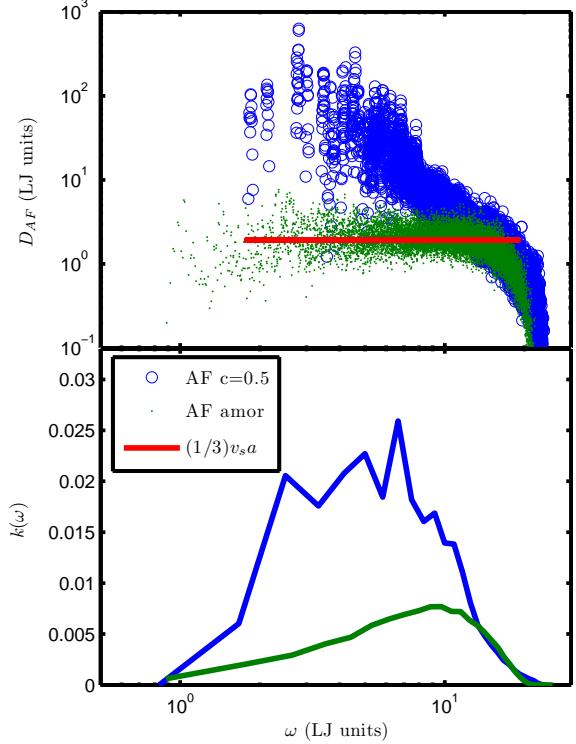


FIG. 4: gamma point results

Molecular dynamics simulations are not able to capture quantum statistical effects.

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

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.

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

High thermal conductivity materials tend to have a conductivity spectrum which is peaked in the low frequency range. It is in this range where the mode lifetimes follow closely the scalings with frequency which can be predicted under the Debye approximation.

It is thus unsurprising that predictions of thermal conductivity for SW silicon using VC-ALD agree well with VC-NMD and GK.

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.

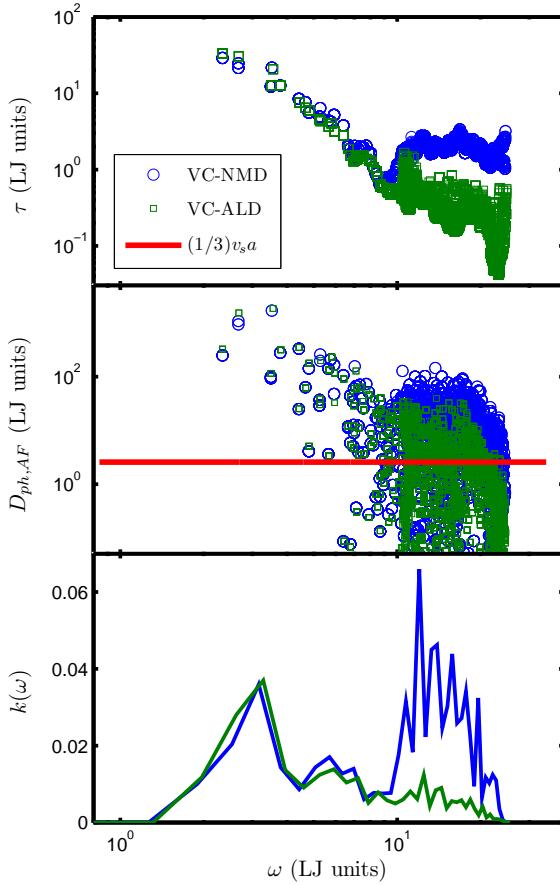


FIG. 5: gamma point results

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.³³

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.^{5,18,19} On the other hand, recent first-principles calculations have shown that the distribution is much narrower for PbTe,²⁰ and thus, further characterizations of the distributions and the associated detailed heat conduction of lead chalcogenides are important for better material design.

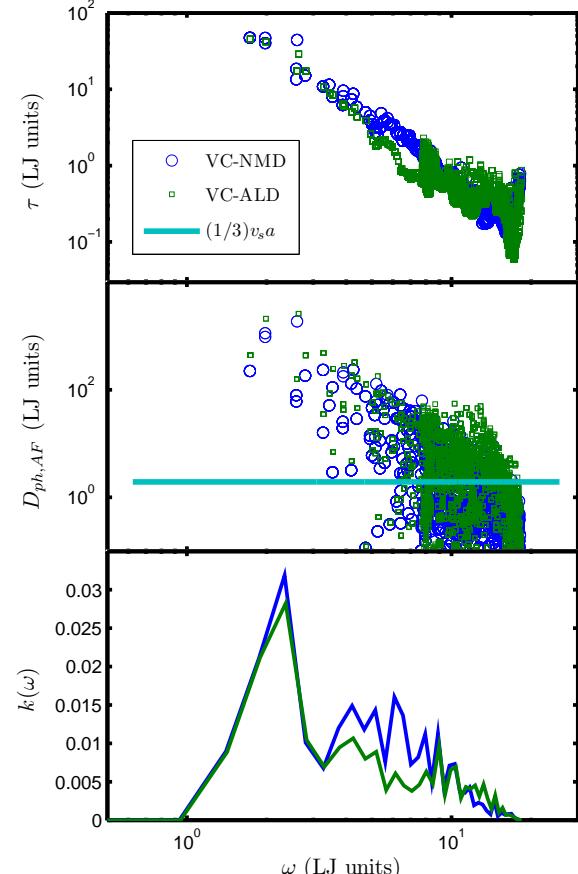


FIG. 6: gamma point results

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

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

where N_{α} and the summations if over the lattice vectors, \mathbf{a}_{α} .? 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

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

where $\mathbf{u}_0(l)$ is the equilibrium position of the l^{th} unit cell and $\mathbf{u}_0(b)$ is the equilibrium position of the b^{th}

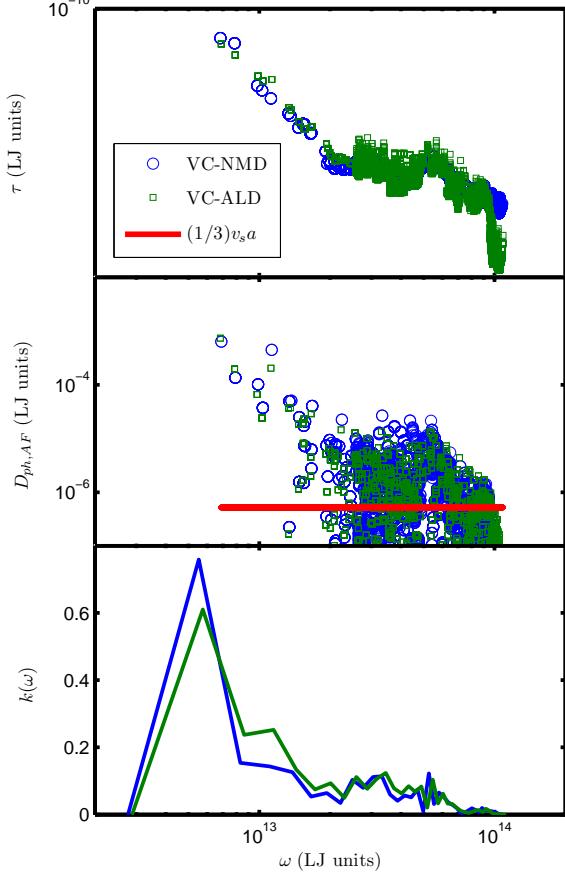


FIG. 7: gamma point results

atom in the unit cell relative to $\mathbf{u}_0(l)$. For the LJ systems studied here, the cubic conventional cells are used with four atoms per unit cell.⁷ For our MD simulations, cubic simulation domains with periodic boundary conditions are used with $N_1 = N_2 = N_3 = N_0$.^{7,8} 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}_{α} are the reciprocal lattice vectors⁷ and $-N_{\alpha}/2 < n_{\alpha} \leq N_{\alpha}/2$, where n_{α} are integers and N_{α} are even integers.⁷ The wavevectors are taken to be in the first Brillouin zone.⁷

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

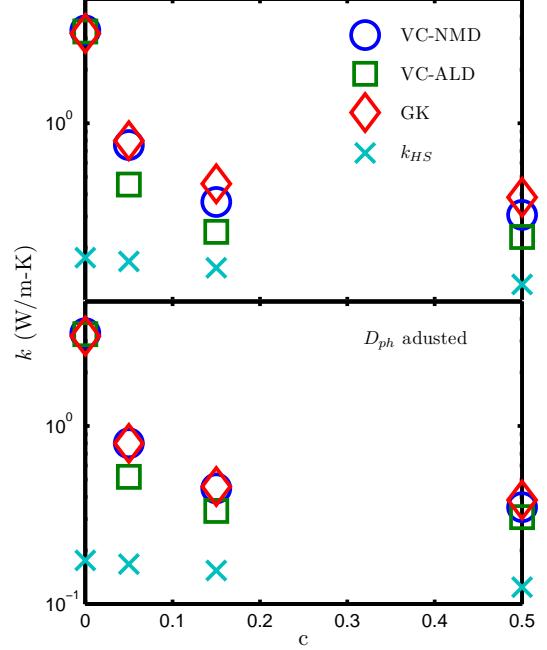


FIG. 8: The vibrational conductivity of LJ alloys predicted using MD simulations and the Green-Kubo method. The predicted thermal conductivities are for a LJ alloy of the form $m_1^a - m_c^b$, where $m^a = 1$, $m^b = 3$, and $m_r = m^a/m^b = 3$ (in LJ units). As the alloy concentration is increased perturbatively,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

this case.

Appendix B: Finite Simulation-Size Scaling for Thermal Conductivity

For the LJ argon system studied in Section ??, a finite simulation-size scaling procedure^{7,9} is used to compare the thermal conductivity predictions from Φ and Φ' to those from the Green-Kubo method. The scaling procedure is demonstrated in Fig. ???. The thermal conductivity is predicted from Φ or Φ' and MD simulations with $N_0 = 4, 6, 8$, and 10 . The bulk conductivity, k_{∞} , is then estimated by fitting the data to

$$1/k = 1/k_{\infty} + A/N_0, \quad (\text{B1})$$

where A is a constant. This procedure is necessary because the first Brillouin zone is only sampled at a finite number of points for a finite simulation size, with no contribution from the volume at its center. To predict a bulk thermal conductivity, it is important to sample points near the Brillouin zone center, where the modes can have large lifetimes and group velocities.^{7,9}

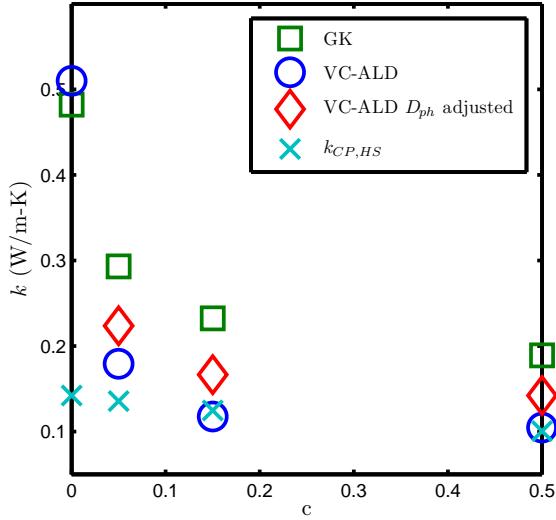


FIG. 9: The vibrational conductivity of LJ alloys predicted using MD simulations and the Green-Kubo method. The predicted thermal conductivities are for a LJ alloy of the form $m_{1-c}^a m_c^b$, where $m^a = 1$, $m^b = 3$, and $m_r = m^a/m^b = 3$ (in LJ units). As the alloy concentration is increased 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.

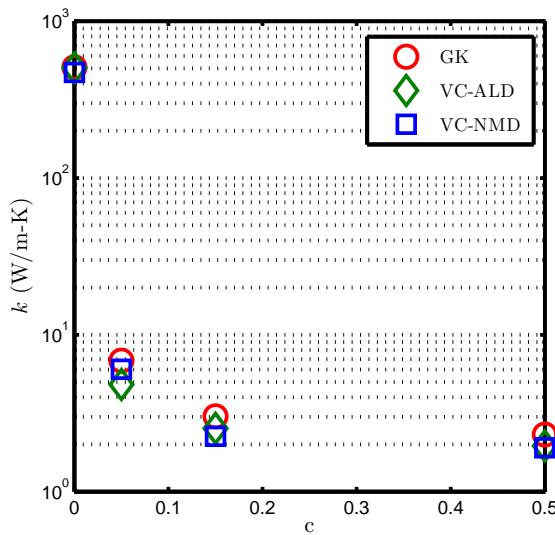


FIG. 10: The vibrational conductivity of LJ alloys predicted using MD simulations and the Green-Kubo method. The predicted thermal conductivities are for a LJ alloy of the form $m_{1-c}^a m_c^b$, where $m^a = 1$, $m^b = 3$, and $m_r = m^a/m^b = 3$ (in LJ units). As the alloy concentration is increased 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.

