

Evaluation of the Virtual Crystal Approximation for Predicting Alloy Phonon Properties and Thermal Conductivity

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(Dated: March 20, 2013)

Abstract

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 frequencies, lifetimes and group velocities and thermal conductivity are predicted. These two alloy systems have different ranges of phonon frequencies and lifetimes. For Stillinger-Weber silicon, the virtual crystal approximation predicts phonon properties and thermal conductivity in reasonably 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 this underprediction is achieved by considering methods that treat the disorder explicitly.

I. INTRODUCTION

Due to their ^{potentially} low thermal conductivities, disordered materials (e.g., alloys, amorphous solids, aerogels) are used in applications ranging from thermoelectric energy conversion to thermally insulating barriers.¹⁻⁶ Disordered lattices are a subgroup of disordered materials where the atomic positions follow a lattice structure but the constituent species are spatially random. Examples include isotopic solids, where the species have the same electronic structure but small mass variations,^{7,8} and alloys, our focus here, where two distinct species are present.^{9,10}

We further restrict our focus to dielectric or semiconducting solids, where the heat is conducted by the atomic vibrational modes. Predicting the thermal conductivity of such materials requires the properties of the full spectrum of vibrational modes.¹¹⁻¹³ Accurate predictions of these properties for crystalline systems (i.e., perfect lattices) can be made with anharmonic lattice dynamics (ALD) theory using input from Density Functional Theory (DFT) calculations.^{8,14-21} Computational costs limit DFT calculations to less than 100 atoms, however, making it challenging to explicitly incorporate the effects of disorder.^{8,15,17,22-24}

Disorder is typically included in the ALD framework using Abeles' virtual crystal (VC) approximation, whereby the disordered solid is replaced with a perfect VC with properties equivalent to an averaging over the disorder (e.g., atomic mass, bond strength).¹⁰ The ALD calculations are performed on a small unit cell with the averaged properties (i.e., all vibrational modes are phonons) and phonon-phonon and phonon-disorder scattering are included as perturbations.^{7,8,10,17}

Except for low-frequency (long-wavelength) acoustic modes, the general validity of this assumption is unclear. We will refer to this approach as VC-ALD. Recent work using DFT calculations and the VC-ALD approach ^{has modeled disordered lattices with} predicted relatively large ($\sim 10\text{-}100\text{ W/m-K}$)^{8,15,20} and small ($\sim 1\text{ W/m-K}$)¹⁷ ~~disordered lattice~~ thermal conductivities. No comprehensive study has been performed to assess the applicability of the VC-ALD approach for a range of disorder strength.

The objective of this study is to investigate the use of the VC approximation for predicting the vibrational mode properties and thermal conductivity of alloys by a detailed comparison of three predictive methods: (i) molecular dynamics (MD)-based normal mode decomposition (NMD), (ii) MD-based Green-Kubo (GK), and (iii) VC-ALD. By using computationally-inexpensive empirical potentials for argon [Lennard-Jones (LJ) at a temperature of 10 K]²⁵

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and silicon [Stillinger-Weber (SW) at a temperature of 300 K],²⁶ we can self-consistently study the effects of disorder both explicitly and as a perturbation. For both materials, the perfect lattice is disordered with a heavier mass species up to equal concentration, spanning a range of perturbative to large disorder. By spanning this range, the limits of the perturbative models are examined.

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The remainder of the paper is organized as follows. In Section II, the theoretical formulation of thermal transport in ordered and disordered solids and the computational framework are ^{described} introduced. In Section III, the frequencies, group velocities, lifetimes, and diffusivities of the vibrational modes of the LJ argon alloys are predicted when the disorder is explicitly modeled and when it is treated as a perturbation in the VC approximation. A breakdown of the VC-ALD method is identified by a comparison with the VC-NMD method in Section III C 2 and a correction is suggested in Section III D. The vibrational mode properties are then used to predict thermal conductivities in Section IV, allowing for a comparison to the predictions of the top-down GK method, where no assumptions about the nature of the thermal transport are required. The vibrational mode properties and thermal conductivity of the SW silicon alloys, where low-frequency modes dominate the thermal conductivity, are predicted in Section V to provide a comparison and contrast to the LJ argon alloys.

II. THEORETICAL AND COMPUTATIONAL FRAMEWORK

A. Thermal Conductivity Prediction

To predict the thermal conductivity of a disordered lattice, one begins with the theory for a perfect lattice. For a perfect lattice, all vibrational modes are phonon modes, which by definition are delocalized, propagating plane waves.¹¹ Using the single-mode relaxation time approximation¹¹ to solve the Boltzmann transport equation²⁷ gives an expression for thermal conductivity in direction \mathbf{n} ,

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

Here, the sum is over the phonon modes in the first Brillouin zone, κ is the wave vector, and ν labels the polarization branch. The phonon mode has frequency $\omega(\kappa_{\nu})$, volumetric specific heat $c_{ph}(\kappa_{\nu})$, \mathbf{n} -component of the group velocity vector $v_{g,\mathbf{n}}(\kappa_{\nu})$, and lifetime $\tau(\kappa_{\nu})$.

The relaxation time approximation has been found to be valid for lower thermal conductivity materials (e.g., Si and SiGe alloys),^{14,15,28} while larger ^{thermal} conductivity materials such as GaN and diamond require an iterative solution to the BTE for more accurate predictions.^{8,29} For the crystalline LJ argon and SW silicon phases, the lattices and the components of their thermal conductivity tensors are cubically symmetric, so that we will refer to k_{ph} as an isotropic scalar thermal conductivity. This isotropy will hold for disordered lattices in the infinite ⁽³¹⁾ size limit. Since MD simulations are classical and obey Maxwell-Boltzmann statistics,³⁰ the volumetric specific heat is k_B/V per mode in the harmonic limit, where V is the system volume. This harmonic approximation has been shown to be valid for LJ argon and SW silicon at the temperatures of interest here ⁽³¹⁾ and is used so that direct comparisons can be made between the MD- and lattice dynamics-based methods. *you didn't show it - cite the papers that did*

For disordered systems, the vibrational modes are no longer pure plane-waves (i.e., phonon modes), except in the low-frequency (long-wavelength) limit. When applied in the classical limit, the Allen-Feldman (AF) theory computes the contribution of diffusive, non-propagating modes (i.e., diffusons) to thermal conductivity from³²

$$k_{AF} = \sum_{\text{diffusons}} \frac{k_B}{V} D_{AF,i}(\omega_i), \quad (2)$$

where $D_{AF,i}$ is the mode diffusivity and ω_i is the frequency of the i th diffuson. The diffusivity of diffusons can be calculated from harmonic lattice dynamics theory.^{12,32,33}

Assuming that all vibrational modes travel with the sound speed, v_s , and scatter over a distance of the lattice constant, a , a high-scatter (HS) limit of thermal conductivity in the classical limit is¹

$$k_{HS} = \frac{k_B}{V_b} b v_s a, \quad (3)$$

where V_b is the volume of the unit cell and b is the number of atoms in the unit cell. The HS limit will be used to discuss the differences between the LJ argon and SW silicon alloys.

B. Virtual Crystal Approximation

Under the VC approximation, the disordered solid is replaced with a perfect, single-species crystal with properties (e.g., density, cohesive energy) equivalent to an averaging over the disorder (e.g., atomic mass, bond strength).¹⁰ The VC approximation is visualized for an alloy in Figs. 1(a) and (b), where a mass-disordered supercell is replaced by a perfect crystal

with an averaged mass. Abeles first introduced the concept of a VC to predict the thermal conductivity of SiGe, ((Ga,In)As and In(As,P) alloys,¹⁰ using Klemens-Callaway theory, to model the phonon-phonon and phonon-defect scattering, which ~~is~~ ^{was used} valid for low-frequency modes and ^{weak} perturbative disorder.^{10,34-38} The Abeles theory is conceptually simple, treating both disorder and anharmonicity as perturbations, and leads to a closed-form analytical function for the thermal conductivity. With the use of phenomenological fitting parameters, good agreement between the predictions and experimental measurements was found for SiGe and GaAs/InAs alloys. Deviations were observed for InAs/InP alloys at large concentrations of InP, which were attributed to the high mass ratio of 3.7 between ~~In~~ ^{indium} and ~~P~~ ^{phosphorus}.¹⁰

When considering alloys, it is important to note that the overall disorder strength is determined by the mass ratio, the stiffness ratio, and the alloy concentration. Cahill and co-workers found that as little as $6.2 \times 10^{19} \text{ cm}^{-3}$ ^{germanium} ~~Ge~~ reduces the thermal conductivity of epitaxial ~~Si~~ ^{silicon} layers by a factor of two.³⁹ Using the Abeles theory, they explained this result by mass perturbative disorder alone (the Ge/Si mass ratio is 2.6).^{39,40} The relative effects of bond and mass disorder were investigated computationally using MD simulations by Skye and Schelling for SiGe alloys up to equal concentration.⁴¹ They also found that mass disorder is the dominant scattering mechanism. Other studies have modeled the effect of differing species by ^{only} including atomic mass difference ~~only~~, which generally captures the effect of scattering on the thermal properties.⁴²⁻⁴⁴ ~~remove Ref 42 - still just LT~~

Unlike the phenomenological Abeles theory, the VC-ALD approach predicts thermal conductivity by directly summing over the modes of the full vibrational spectrum, with phonon-phonon and phonon-defect scattering treated as perturbations.^{8,15,17} In the VC-ALD method, the phonon-phonon scattering is predicted using ALD.^{19,45} The phonon-defect scattering is treated using perturbative methods that can handle mass and/or bond disorder and recover the Klemens theory predictions (e.g., $\tau \sim \omega^{-4}$) at low-frequencies^{7,34,35,37} In $\text{Ni}_{0.55}\text{Pd}_{0.45}$, which has a large mass ratio (1.8) and concentration of each species, experimental measurements of vibrational frequencies and linewidths agree well with predictions from the perturbative mass disorder theory.^{7,37,38}

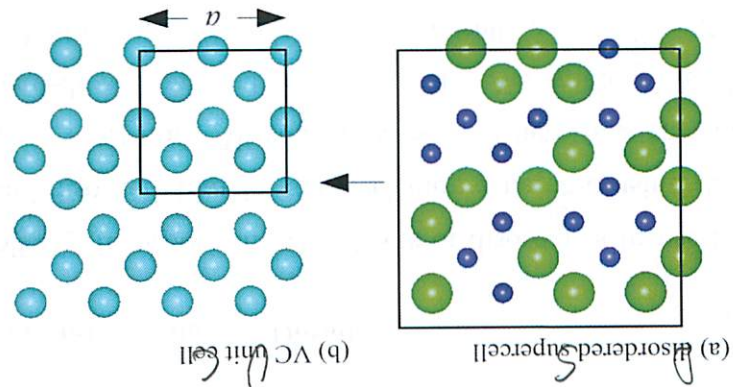
Using DFT methods to predict the mode-specific phonon properties of the VC, Lindsay and Broido found good agreement between VC-ALD and experimental measurements of thermal conductivity for isotopically defected GaN ^{gallium} (isotope concentration of 0.6 and mass ratio of 1.03).⁸ Garg et al. used DFT calculations with VC-ALD to predict the thermal

conductivity of SiGe alloys for all concentrations at a temperature of 300 K, obtaining good agreement with experiment.¹⁵ Isotopically-defected GaN and low concentration SiGe alloys have relatively large thermal conductivities at a temperature of 300 K (~ 100 W/m-K). Li et al. used DFT calculations with VC-ALD to predict the thermal conductivity of $\text{Mg}_2\text{Si}_x\text{Sn}_{1-x}$ (~ 10 W/m-K) in good agreement with experimental measurements for all concentrations.²⁰ The VC-ALD approach has also been used to predict the effect of ~~mixing~~ ^{interplay} in GaAs/AlAs superlattices, but ^{the} thermal conductivity predictions were not compared with experimental measurements.²¹ In our survey of experimental measurement and numerical modeling, we find that VC predictions tend to be accurate when the disordered lattice thermal conductivity is significantly above the high-scatter limit [Eq. (3)] which tends to be around 1 W/m-K.^{1,8,10,15,38-40} ^{can you be more specific?}

An ALD study using phonon properties from DFT calculations for crystalline PbTe¹⁶ predicted thermal conductivities (~ 1 W/m-K) for the perfect systems in fair agreement with experiment. For PbTeSe alloys, a VC-ALD study predicted a small thermal conductivity reduction compared to the perfect crystals ^{needed?} (with increasing concentration).¹⁷ Experimental results ^{are limited} ~~lack~~ for these alloys,^{46,47} making it difficult to assess the validity of the VC-ALD approach for ~~these~~ materials whose thermal conductivities approach the HS limit.⁴⁸

Given all these results, it is unclear what limitations exist ^{for} using the VC approach. In this study, we will consider a low thermal conductivity alloy using the LJ potential and a high thermal conductivity alloy using the SW potential. The computational studies discussed above were limited to VC-ALD because of DFT calculation costs. Our use of computationally inexpensive empirical potentials allows us to include the disorder explicitly and as a perturbation and to compare the predictions.

FIG. 1: (a) Explicitly disordered supercell of Si and "heavy" Si ([100] direction into the paper).
 (b) Equivalent VC supercell with one averaged mass. The sphere size represents increasing mass only, no bond disorder is considered. The 8-atom conventional cubic unit cell is shown in (b).



C. Calculation and Simulation Details

The key to explicitly incorporating the effects of disorder is to use large disordered supercells. Perfect and disordered lattice supercells are generated using the conventional unit cells for LJ argon ($n = 4$) and SW silicon ($n = 8$), where n is the number of atoms in the unit cell. Supercells are built cubically with size N_0 , where N_0 is the number of unit cell repetitions in all three spatial directions. Supercells up to $N_0 = 12$ (6,096 atoms) are used for the LJ argon calculations. For SW silicon, $N_0 = 8$ (4,096 atoms) is used for the MD-based NMD calculations and $N_0 \leq 42$ (592,704 atoms) is used for the MD-based GK and VC-ALD.

Disorder is created by randomly specifying the masses of the atoms on the lattice. The composition of each lattice is labeled by $m_{1-c}^i m_c^j$, where (i) $m^i = 1$ and $m^j = 3$ in LJ units for argon, and (ii) $m^i = m_{Si}$ and $m^j = 2.6m_{Si}$ for SW silicon and “heavy silicon”, which has the mass of germanium. Concentrations, c , of 0, 0.05, 0.15 and 0.5 are considered.

For LJ argon, the lattice constant at a temperature of 10 K is 5.290\AA .⁵⁰ The MD simulations were performed using LAMMPS.⁵¹ Efficient MD codes like LAMMPS scale linearly with the number of atoms in the system, N_a , which makes the GK method (see Section IV) computationally-inexpensive when used with empirical potentials. An amorphous LJ phase, discussed in Section III D, was created by liquefying the crystal and instantly quenching by removing all kinetic energy. The energy of the resulting structure was minimized and then annealed in an NPT (constant number of atoms N , pressure P , and temperature T) ensemble at zero pressure and a temperature of 10 K. The effective zero-pressure lattice constant of the amorphous phase at this temperature, based on the atomic density, is 5.389\AA .⁽⁵⁰⁾ For SW silicon, we use a lattice constant of 5.43\AA for all calculations, which brings the GK thermal conductivity predictions at a temperature of 300K ^(52,53) into agreement with ~~the~~ ALD predictions⁵⁴ compared to the zero-pressure lattice constant. using

All MD simulations are first equilibrated in a NVT (constant number of atoms, volume, and temperature) ensemble for 10^6 time steps. Data is then collected from simulations in the NVE (constant number of atoms, volume, and total energy) ensemble. For LJ argon, the potential energy is cutoff and shifted at 8.5\AA (the force is not adjusted). Time steps of 4.285 and 0.5 fs were used for the LJ argon and SW silicon simulations. The same atomic trajectories are used for the NMD and GK methods.

III. VIBRATIONAL MODE PROPERTIES IN ALLOYS

A. ~~Virtual Crystal and Gamma~~ Density of States

In this section, we begin to examine the effects of explicitly including disorder by computing the frequencies and density of states (DOS) for the vibrational modes of disordered LJ lattice supercells and their equivalent VCs. The frequencies are computed using harmonic lattice dynamics calculations with GULP.⁵⁵ For the VC, the allowed wave vectors are set by N_0 and, due to the use of the conventional unit cell, there are 12 polarization branches per wave vector. For the disordered supercells (referred to herein as Gamma), the only allowed wave vector is the gamma-point (i.e., $\kappa = 0$), where there are $12N_0^3$ polarization branches. Calculation of the Gamma modes require the eigenvalue solution of a ~~large~~ dynamical matrix of size $(3N_a)^2$ that scales as $[(3N_a)^2]^3$ and limits the system sizes considered. This eigenvalue solution is also required to perform the Gamma-NMD (see Section III C 1) and AF calculations (see Section III D).

The DOS for the VC and Gamma modes are plotted in Figs. 2(a), 2(b), and 2(c) for concentrations of 0.05, 0.15 and 0.5 for $N_0 = 12$ (6,912 atoms). The VC and Gamma DOS agree at low frequencies for all concentrations, where they follow the prediction of the Debye approximation that the DOS will scale as ω^2 .²⁵ Similar agreement between VC and Gamma DOS at low frequencies was found in DFT predictions for $\text{Si}_c\text{Ge}_{1-c}$ ¹⁵ and classical models of amorphous $\text{Si}_c\text{Ge}_{1-c}$.⁵⁶ The Debye approximation underpredicts the DOS at moderate frequency, which is due to non-linearities in the dispersion,²⁵ but the VC and Gamma predictions remain in good agreement.

The increasing average atomic mass with increasing concentration for the VC shifts all frequencies downward by a factor $1/[(1-c)m^i + cm^j]^{1/2}$. The increasing average atomic mass for the Gamma modes also reduces the frequencies, but not in a systematic manner. The effect of the disorder is seen at frequencies greater than ten by a broadening and shift of the Gamma DOS to higher frequencies because of the explicit use of light atoms in the supercell. This effect becomes more pronounced as the concentration increases. Duda et al. observed similar high-frequency broadening effects in model LJ alloys.⁵⁷ The high-frequency broadening is an indication of phonon localization, which is known to occur first at the phonon band edge.⁵⁸ Based on the DOS, the vibrational modes of the explicitly disordered

2. Brillouin zone edge?

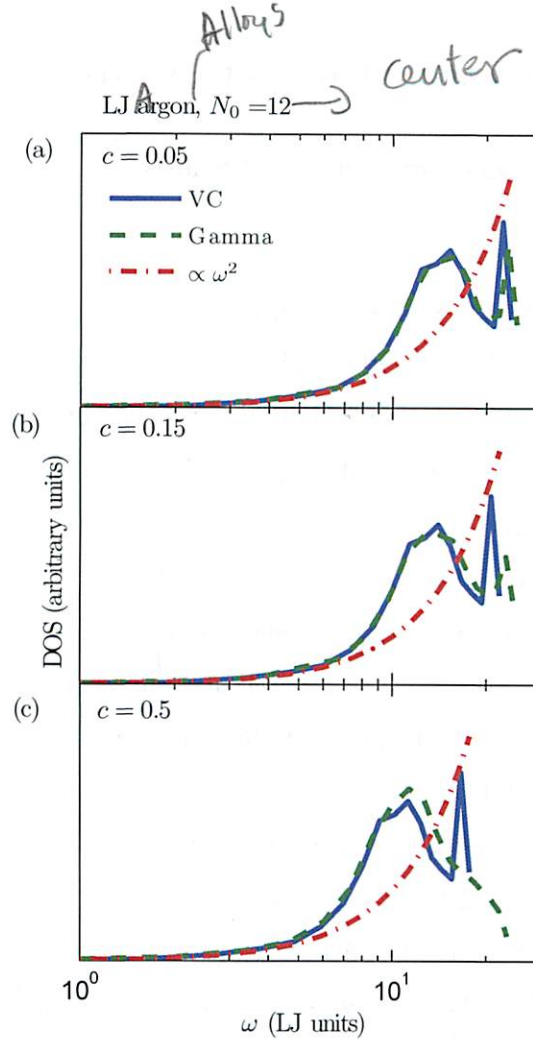


FIG. 2: Vibrational DOS for LJ alloys calculated using the VC approximation and an explicitly disordered supercell (labeled Gamma) for concentrations (a)0.05, (b)0.15, and (c)0.5. VC and Gamma show similar low-frequency behavior for all concentrations. For increasing concentrations, the frequencies of both VC and Gamma decrease, while the high frequency DOS for Gamma spreads and reaches to a higher maximum frequency because of the explicit disorder. The ~~the~~ supercells are of size $N_0 = 12$ (6,912 atoms).

supercells at low frequencies are phonon-like, while the broadening of the DOS at high-frequency indicates that the Gamma vibrational modes may differ from the VC phonon modes in this regime. This behavior is further investigated in the next three sections.

B. Dispersion and Group Velocity

The group velocity vector in a VC is defined as the gradient of the dispersion curve,

$$\text{vector! } v_{g,n}(\kappa) = \frac{\partial \omega(\kappa)}{\partial \kappa}. \quad (4)$$

We calculate the group velocities for the VC using finite differences on the frequencies calculated from harmonic lattice dynamics.⁵⁹

For a disordered solid, the three acoustic group velocities (two transverse and one longitudinal) can be predicted using the elastic constants⁵⁵ or by finite differencing of the three lowest frequency branches of the dispersion relation of the supercell.^{60,61} Except for this low-frequency behavior, there is not an accepted method to predict the group velocity of a vibrational mode in a disordered system, although there have been attempts.^{1,57,60-62} In the Cahill-Pohl (CP) model, for example, the group velocity of all disordered modes is the sound speed, v_s , which is also assumed for the HS model, Eq. (3).¹ ~~However,~~ This assumption is ~~not good~~ ^{generally valid} for any material.^{33,57,60-62}

Calculating the structure factors of the supercell Gamma modes is a method to test for their plane-wave character at a particular wave vector and polarization corresponding to the VC.^{13,33} Feldman et al. used the structure factor to predict an effective dispersion for a model of amorphous silicon, but did not predict group velocities.³³ Volz and Chen used the dynamic structure factor to predict the dispersion of crystalline SW silicon using MD simulation.⁶³

The structure factor at a ~~virtual crystal~~ ^{VC} wave vector κ_{VC} is defined as¹³

$$S^{L,T}(\kappa_{VC}) = \sum_{\nu} E^{L,T}(\kappa_{VC}) \delta[\omega - \omega(\kappa_{\nu}^0)], \quad (5)$$

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

$$E^L(\kappa_{VC}) = \left| \sum_b \hat{\kappa}_{VC} \cdot e(\kappa_{\nu}^0)_b \exp[i\kappa_{VC} \cdot \mathbf{r}_0^{(l=0)}_b] \right|^2 \quad (6)$$

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

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

In Eqs. (6) and (7), the b summations are over the atoms in the disordered supercell, $\mathbf{r}_0^{(l=0)}_b$ refers to the equilibrium atomic position of atom b in the supercell, l labels the ~~different~~ unit.

cells ($l = 0$ for the supercell), α labels the Cartesian coordinates, and $\hat{\kappa}_{VC}$ is a unit vector. Explicit disorder is included in the Gamma frequencies $\omega(\kappa=0)$ and the $3N_a$ components of the eigenvectors $e(\kappa=0)_\alpha$.

Physically, $S^{L,T}(\omega)$ represents the frequency spectrum required to create a wavepacket with a well-defined wave vector and polarization.^{13,33,64} For a perfect lattice, the structure factor peaks are delta functions centered at the mode frequencies, indicating that the modes are pure plane-waves (i.e., phonons). A sampling of the structure factors for the LJ argon alloys are plotted in Fig. 3 for wave vectors along the [100] and [111] directions in the $N_0 = 10$ systems.⁶⁵ Well-defined peaks at all wave vectors are due to the lattice structure of the disordered systems. Typically, the structure factor for amorphous materials has well-defined peaks only for small wave vector.^{13,33} With increasing disorder, the structure factor spreads in width, particularly at high frequencies, which is an indication that the modes are not pure plane waves.

From Fig. 3, an effective dispersion curve (middle panels) can be extracted by locating the peaks in the structure factors at neighboring VC wave vectors. The peaks in the structure factor are larger than the VC predicted frequencies (plotted as solid lines in Fig. 3) by at most 5%. Similar agreement is found with the disordered SW silicon lattice supercells.

Even though there is good agreement between the VC-predicted dispersion curves and the peaks in the structure factors from Fig. 3, the effect of the width of the peaks is not clear. We will 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. ~~We will discuss~~ ^T the validity of this group velocity choice ⁱⁿ Section III E.

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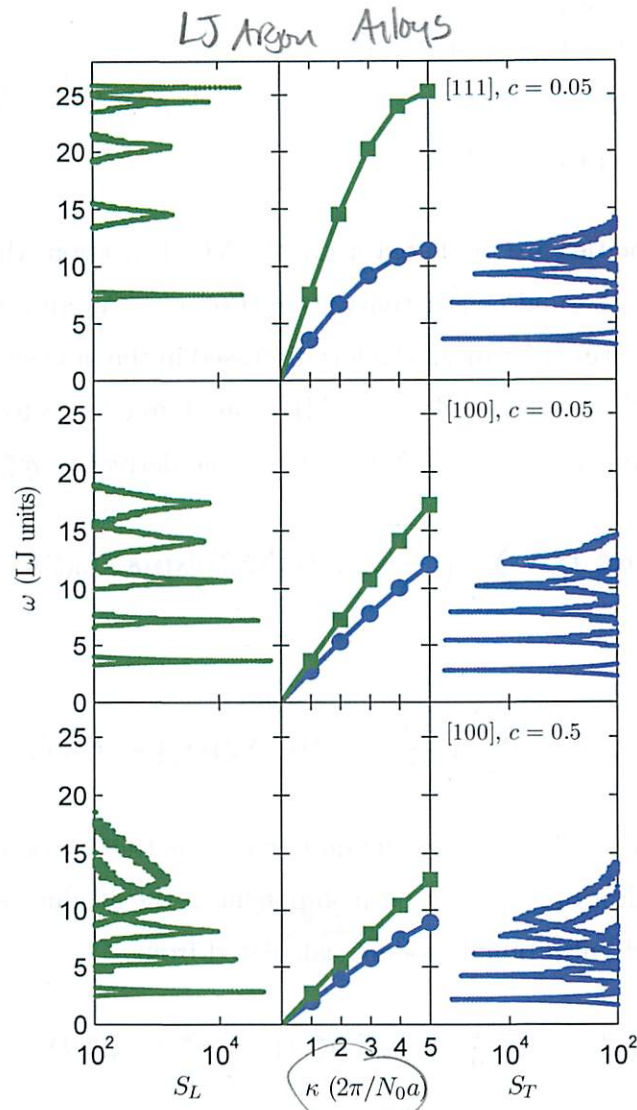


FIG. 3: Left and Right Panels: The structure factor for longitudinal (S_L) and transverse (S_T) polarizations along high-symmetry directions of the mass disordered LJ argon supercells ($N_0 = 10$, $c = 0.05, 0.5$). Center Panels: The VC predicted dispersion curves (solid lines) agree well with the peaks in S_L and S_T .

C. Lifetimes

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1. From VC-NMD and Gamma-NMD

Once the group velocities are predicted using the VC dispersion, the mode lifetimes are required to predict the thermal conductivity using Eq. (1). As an alternative to the VC-ALD approach for predicting lifetimes, which is discussed in the next section, we first use the MD simulation-based NMD method.^{66,67} In NMD, the atomic trajectories are first mapped onto the vibrational mode coordinate $q(\kappa; t)$ and its time derivative $\dot{q}(\kappa; t)$ by⁶⁸

$$q(\kappa; t) = \sum_{\alpha, b, l}^{3, n, N} \sqrt{\frac{m_b}{N}} u_{\alpha}(l; t) e^*(\kappa \frac{b}{\alpha}) \exp[i\kappa \cdot \mathbf{r}_0(l)] \quad (8)$$

and

$$\dot{q}(\kappa; t) = \sum_{\alpha, b, l}^{3, n, N} \sqrt{\frac{m_b}{N}} \dot{u}_{\alpha}(l; t) e^*(\kappa \frac{b}{\alpha}) \exp[i\kappa \cdot \mathbf{r}_0(l)]. \quad (9)$$

Here,

where m_b is the mass of the b_{th} atom in the unit cell, u_{α} is the α -component of the atomic displacement from equilibrium, \dot{u}_{α} is the α -component of the atomic velocity, and t is time. The total energy of each vibrational mode $E(\kappa; t)$ is calculated from

$$E(\kappa; t) = \frac{\omega(\kappa)^2}{2} q(\kappa; t)^* q(\kappa; t) + \frac{1}{2} \dot{q}(\kappa; t)^* \dot{q}(\kappa; t). \quad (10)$$

The vibrational mode lifetime is predicted using

$$\tau(\kappa) = \int_0^{t^*} \frac{\langle E(\kappa; t) E(\kappa; 0) \rangle}{\langle E(\kappa; 0) E(\kappa; 0) \rangle} dt, \quad (11)$$

where the upper integration limit t^* is set to be much larger than the mode lifetime and the brackets indicate an ensemble average.³¹ Equation (11) is derived by assuming that the energy autocorrelation follows an exponential decay. ⁶⁷ → does Ladd also use this formula?

We perform the MD simulations using the fully disordered supercell⁵ and project onto the frequencies and eigenvectors from both the VC unit cell $[\omega(\kappa), e(\kappa \frac{b}{\alpha})]$ and the Gamma supercell $[\omega(\kappa=0), e(\kappa=0 \frac{b}{\alpha})]$. The trajectories from these MD simulations are also used in the GK method calculations (Section IV). The MD simulations were ten times longer than the longest lifetime in the system, which was estimated from the VC-ALD predicted lifetimes. For LJ argon and SW silicon, data was collected 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 of the energy autocorrelations was performed using ten independent, initially-randomized velocity distributions.

For the normal modes of the lattice supercell, Eq. (11) is exact, but this expression becomes an approximation when using the VC normal modes to perform the mappings in Eqs. (8) and (9). Even for larger disorder ($c = 0.5$), where the energy autocorrelations deviate from an exponential decay, an effective lifetime can still be predicted using Eq. (11) (see Appendix A). The lifetimes predicted using VC-NMD and Gamma-NMD are shown in Figs. 4(a)-(d) for the LJ argon crystal and all alloys at a temperature of 10 K. The range of frequencies for VC-NMD and Gamma-NMD differ slightly due to differences in the DOS (see Fig. 2). For a small interval of frequency, there is a wider range of predicted lifetimes for Gamma-NMD. This spread is because there is no symmetry-averaging of the mode properties, which is possible for the VC by considering the crystal lattice's irreducible Brillouin zone (BZ).²⁵ *used anywhere else? if not, no need for abbreviation*

The lifetimes predicted by both VC-NMD and Gamma-NMD show a ω^{-2} scaling at low frequency and a ω^{-4} scaling (for the alloys) and even faster for mid-range frequencies. The ω^{-2} scaling is due to three-phonon scattering processes^{36,69} and can also be seen in VC-ALD predicted lifetimes (see Fig. 5(a)). The ω^{-4} scaling is due to the ~~phonon~~ mass point defects. *scattering (REP)* These low- and mid-frequency scalings are predicted by the perturbative models used by the VC-ALD method (see Section III C 2). A constant lifetime is observed at the highest frequencies for both VC-NMD and Gamma-NMD except at $c = 0.5$ for VC-NMD. We are not aware of any theoretical prediction of this high-frequency behavior. However, prediction of a high-frequency plateau of the vibrational mode diffusivities (see Section III D) for a model disordered lattice were explained by a plateau in the vibrational mode lifetimes.⁷⁰ *this comment breaks the flow*

The majority of the lifetimes predicted by both VC-NMD and Gamma-NMD are larger than the Ioffe-Regel (IR) limit,⁷¹

$$\tau = \frac{2\pi}{\omega}. \quad (12)$$

The physical interpretation of the IR limit is a mode that scatters in a time equal to its oscillation period. Our results suggest that the IR limit is a good lower-limit for the lifetimes predicted by VC-NMD and Gamma-NMD for LJ argon (Fig. 4) and VC-NMD for SW silicon [see Fig. 8(a) in Section V].

Overall, good agreement is seen in the predicted lifetimes from VC-NMD and Gamma-

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NMD in both magnitude and trends. The use of the VC normal modes is an approximation that becomes worse as the concentration is increased (see Appendix A), but our results suggest that the effect is only pronounced at the highest frequencies and at high alloy concentration. The only approximation associated with Gamma-NMD is the use of the harmonic lattice dynamics-predicted frequencies and eigenvectors to map the atomic trajectories from the fully anharmonic MD simulations. This assumption has been shown to be valid for LJ argon below temperatures of 40 K.⁶⁷ Based on the good agreement with Gamma-NMD, the ~~lifetimes predicted by VC-NMD~~ are used along with the VC ~~normal modes~~ group velocities to predict thermal conductivity in Section IV. For Gamma-NMD, there is no accepted way to predict the mode group velocities, so that the thermal conductivity cannot be predicted using Eq. (1).

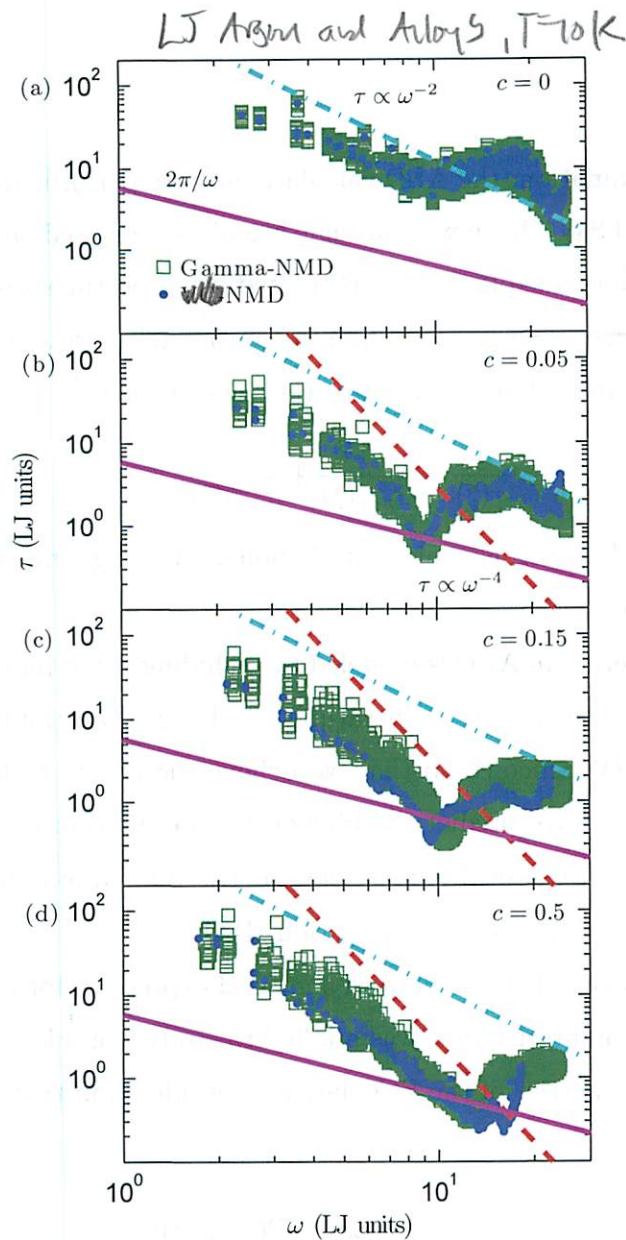


FIG. 4: Lifetimes predicted using VC-NMD and Gamma-NMD from MD simulations of (a) perfect LJ argon and (b),(c),(d) mass-disordered LJ alloys. Good agreement in trends and magnitude is seen comparing VC-NMD to Gamma-NMD. Both ω^{-2} and ω^{-4} scalings can be observed at low frequencies, which are predicted by the perturbative models used for VC-ALD (Section III C 2). For both VC-NMD and Gamma-NMD, most mode lifetimes are greater than the Ioffe-Regel limit $\tau = 2\pi/\omega$.⁷¹ While there is more “noise” in the Gamma-NMD data (Section III C 1), the lifetime magnitudes and trends agree well, an important consideration when comparing VC-NMD and VC-ALD in Fig. 5 (a).

2. From VC-ALD

Under the VC approximation, the ALD calculations⁶⁷ are performed on the conventional unit cells of LJ argon and SW silicon with a single atomic mass based on the alloy concentration. Disorder is not included explicitly but is treated using perturbation theory. Assuming ~~phonon-phonon and phonon-defect~~ scattering mechanisms to operate independently, the effective phonon lifetime can be found using the Matthiessen rule,¹¹

$$\frac{1}{\tau(\kappa)} = \frac{1}{\tau_{p-p}(\kappa)} + \frac{1}{\tau_{p-d}(\kappa)}, \quad (13)$$

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

Phonon-phonon scattering in ALD is modeled by including three-phonon processes.^{15,17,67} The present study is concerned with temperatures much less than the melting temperature of either LJ argon⁵⁰ or SW silicon²⁶ so that we believe the effects of higher-order phonon processes are negligible.^{67,72} We predict the phonon-phonon lifetimes using the method described in Ref. 67, with all classical expressions for the populations to remain consistent with the classical MD-based methods from Section III C 1.

Using perturbation theory, Tamura derived a general expression for phonon scattering by mass point defects to second order that was applied to study isotopic germanium.⁷ By considering the symmetry properties of the FCC lattices considered in this work, his expression reduces to

$$\frac{1}{\tau_{p-d}(\kappa)} = \frac{\pi}{2} g_2 \omega^2(\kappa) \text{DOS}[\omega(\kappa)], \quad (14)$$

where

$$g_n = \sum_{\mu} c^{\mu} (1 - m^{\mu} / \bar{m}^{\mu})^n. \quad (15)$$

Here, c^{μ} and m^{μ} are the concentration and mass of the μ -th species and \bar{m}^{μ} is the average mass. Bond disorder can be accounted for using a similar expression with an average atomic radius or suitable scattering cross-section.^{34,35} For the binary LJ argon and SW silicon alloys considered here, there is one atom type in the unit cell with $\mu = i, j$, so that the alloying atom labeled by m_c^i can be considered to be an “isotope” of the atom labeled m_{1-c}^j . ~~The disordered lifetimes are calculated using Eqs. (14) and (15).⁷³~~

$m_c^i = 1$?

The lifetimes predicted by VC-ALD for LJ argon at a concentration of 0.05 are plotted in Fig. 5(a). Also plotted are the lifetimes for the perfect system and from the VC-NMD predictions [Fig. 4(b)] at this concentration. At low frequencies, where the DOS is Debye-like [$D(\omega) \propto \omega^2$, Fig. 2], $\tau_{p-p}(\frac{\omega}{v})$ scales as ω^{-2} , ^a The scaling ~~is~~ also observed in the VC-NMD and Gamma-NMD lifetimes. Under the Debye-approximation, the phonon scattering due to mass point-defects is predicted to scale as ω^{-4} from Eq. (14), ^{7,37} ~~and~~ ^{this scaling is} observed in the VC-NMD, Gamma-NMD and VC-ALD predicted lifetimes in the mid-frequency range. VC-ALD does not predict the frequency-independent lifetimes at high frequency for LJ argon observed in VC-NMD and Gamma-NMD.

The Tamura theory was developed to predict the reduction of lifetimes in isotopic germanium, which is only perturbatively disordered ($\sim 5\%$ variation in the atomic masses). In the LJ alloys, the masses differ by a factor of three. Large mass ratios were also considered in the DFT VC-ALD studies of SiGe (mass ratio of 2.6)¹⁵, PbTeSe (2.6)¹⁷, and MgSiSn (4.9)²⁰. The importance of higher-order interactions in the Tamura theory can be estimated by the disorder strength (i.e., g_n for $n > 2$).⁷ For isotopically-disordered germanium, Tamura estimated that the higher-order contributions were negligible ($g_2 = 5.87 \times 10^{-4}$, $g_3 \sim 10^{-7}$ and $g_4 \sim 10^{-7}$).⁷ For LJ argon and a concentration of 0.15, $g_2 = 0.3018$, $g_3 = -0.3250$ and $g_4 = 0.4411$. It is possible that the neglect of the higher-order interactions in the Tamura theory is responsible for the discrepancy of the lifetimes predicted by VC-NMD and Gamma-NMD versus VC-ALD at high frequency.

The lifetimes predicted by ~~VC-NMD~~ ^{VC-NMD} and ~~VC-ALD~~ ^{VC-ALD} for the perfect LJ argon crystal agree within 20% ^{on a} mode-by-mode ^{basis} and the ~~predicted~~ ^{results} thermal conductivities agree within the ~~errors~~ ^{if contributions} (see Table I). Evaluation of the higher-order interactions in the Tamura theory is of similar complexity to anharmonic phonon interactions for ~~$n > 3$~~ ^(67,72) and is beyond the scope of this work.

Full

- comment that VC-ALD is full below IR at high ω

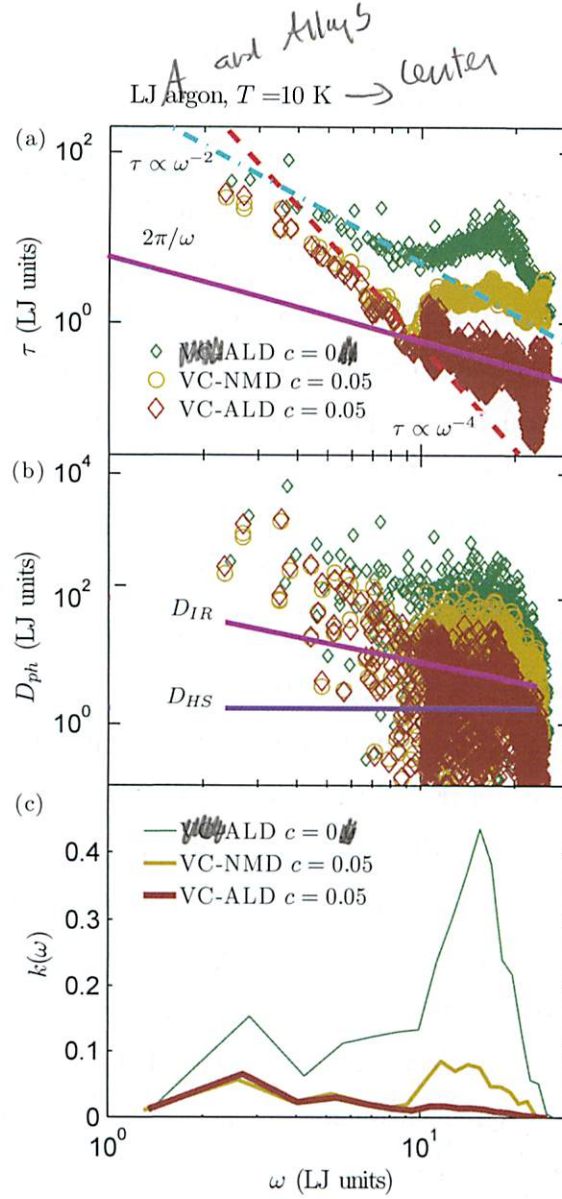


FIG. 5: (a) Predicted lifetimes using VC-NMD and VC-ALD for LJ argon ($T = 10$ K, $N_0 = 10$, and $c = 0.05$). (b) predicted VC-M mode diffusivities compared to the HS limit, D_{HS} [Eq. (18)]_f and the IR limit, D_{IR} [Eq. (19)]. VC-NMD and VC-ALD predict a large number of high-frequency modes with $D_{ph} < D_{HS}$. (c) the thermal conductivity frequency spectrum, which is peaked at high frequency, in contrast to SW silicon [Fig 8(c)].

D. Diffusivities

We now use the AF theory to provide a lower limit for the contribution of a given vibrational mode to thermal conductivity (within the computational framework of the VC approximation). While studies have been performed on alloying the amorphous phase,¹² the AF theory has not been previously applied to disordered lattices. In the classical harmonic limit for specific heat, a mode's contribution to the thermal conductivity ~~is~~ is determined by its diffusivity,

$$D_{ph,n}(\kappa) = v_{g,n}^2(\kappa) \tau(\kappa), \quad (16)$$

such that from Eq. (1)

$$k_{ph,n} = \sum_{\kappa} \sum_{\nu} \frac{k_B}{V} D_{ph,n}(\kappa). \quad (17)$$

The lower limit for phonon diffusivity is zero since the group velocities can be zero (e.g., optical modes at the Brillouin zone center).

In a disordered system, modes can transport heat by harmonic coupling in the AF theory of diffusons.³² In the HS limit,¹ the diffusivity of each mode is

$$D_{HS} = \frac{1}{3} v_s a, \quad (18)$$

which leads to Eq. (3).⁷⁴ The physical interpretation of Eq. (18) is that all vibrational modes transport heat at the sound speed and have a mean free path of the lattice spacing. Based on the IR limit, another possible lower-bound of diffusivity is

doesn't make sense - what assumption? $D_{IR} = \frac{2\pi}{3} \frac{v_s^2}{\omega},$ Not applicable

which is the ~~assumption made in the Cahill-Pohl (CP) model.~~¹ As seen in Fig. 5(b) for the LJ argon alloy at a concentration of 0.05, VC-NMD and VC-ALD predict [from Eq. (16)] a significant number of modes with $D_{ph}(\kappa)$ less than D_{HS} , and D_{IR} approaches D_{HS} at high frequency.⁷⁵ For both VC-NMD and VC-ALD, we approximate $v_{g,n}(\kappa)$ from the VC dispersion (Section III B) so that any differences in ~~diffusivity~~ D_{ph} will come from the predicted lifetimes. ~~We use the x-component of the group velocity to predict the mode diffusivities.~~
 using the x-component of group velocity
 integrate here

While the HS model assumes a mode-independent diffusivity, the AF theory is capable of predicting mode-specific thermal diffusivities D_{AF} ~~Eq. 16~~.^{12,33,75} Since the AF theory is harmonic, the diffusivities typically diverge as the frequency approaches zero because these

vibrations are long-wavelength plane waves that are weakly scattered by the disorder.^{76,77}

The mode-specific diffusivities of an LJ argon amorphous phase⁷⁸ are plotted in Fig. 6 along with the HS limit, D_{HS} . The sound speed is estimated by

$$v_s = \frac{1}{3}v_{s,L} + \frac{2}{3}v_{s,T}, \quad (20)$$

where $v_{s,L}$ and $v_{s,T}$ are the longitudinal and transverse sound speeds calculated from the elastic constants,⁵⁵ which agree within 20 % with the branch-averaged sound speeds along the high-symmetry dispersion directions [100], [110], and [111]. Except at the highest frequencies,

the diffusivity of all amorphous modes can be approximated using a mode-independent diffusivity D_{HS} . Also plotted in Fig. 6 are diffusivities predicted from the AF theory for the explicitly-disordered LJ argon lattice supercell alloy at a concentration of 0.5. As expected, the AF theory predictions diverge at low frequency.⁷⁹ The diffusivity of all modes are larger than D_{HS} except at the highest frequencies, where they tend to zero as with the amorphous phase. This result supports the hypothesis that the lower-bound of the VC predicted phonon diffusivity should be D_{HS} , which is further explored in Sections IV and V.

— Comment on DFR in Fig. 6 → clearly not a lower limit
(and not zero)

give the value of v_s

this comment should appear after Eq. (18)

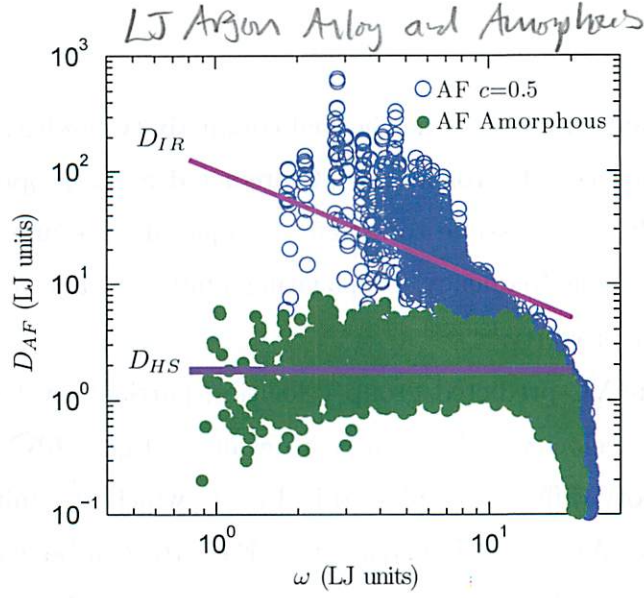


FIG. 6: AF theory predictions of disordered mode diffusivities for LJ argon alloy and amorphous phases. The thermal conductivity of the amorphous phase is well-described by a mode-independent diffusivity D_{HS} [Eq. (18)]. The system size for the alloy is $N_0 = 10$ (6,912 atoms), and the amorphous phase has 6,912 atoms.

E. Discussion

In this section, in anticipation of the thermal conductivity predictions in Section IV, we discuss two possible sources of error in the VC-predicted mode properties. For disordered systems, it is generally only possible to assign a unique lifetime and group velocity to vibrational modes in the low-frequency, propagating limit.^{33,80} The mode diffusivity is the fundamental transport property.^{12,32,33}

We believe that the VC-predicted group velocities, particularly for $v_{g,n}(\frac{\kappa}{\nu}) \approx 0$, are an underprediction of the velocity scale required to evaluate Eq. (16). This statement is supported by the AF-theory diffusivities plotted in Fig. 6, which are finite for the LJ alloy at a concentration of 0.5. While the diffusivity from Eq. (16) can be zero because of the VC-predicted group velocities, this result is not consistent with the AF theory predictions.

The VC-NMD and Gamma-NMD predicted lifetimes are generally larger than the IR limit for LJ argon and its alloys (see Fig. 4). The constant lifetime observed at the highest frequencies for both VC-NMD (except at $c = 0.5$) and Gamma-NMD is consistent with the plateau of mode diffusivity at high frequency predicted for a model disordered lattice.⁷⁰ VC-ALD predicts essentially monotonically decreasing lifetimes with increasing frequency for the LJ argon alloys [Fig. 5(a)] with many falling below the IR limit. Because VC-NMD and VC-ALD use the same values for $v_{g,n}(\frac{\kappa}{\nu})$, the mode diffusivities will therefore be underpredicted for VC-ALD compared to VC-NMD for the LJ argon alloys.

IV. THERMAL CONDUCTIVITY PREDICTIONS

The thermal conductivities of the LJ systems can now be predicted from Eq. (1) using the vibrational mode properties from VC-NMD and VC-ALD. Given the discussion regarding the VC-predicted mode properties in Section III E, we also predict thermal conductivity using the equilibrium MD-based GK method, which is a top-down method that does not make any approximations about the nature of the vibrational modes. Thermal conductivities predicted by the GK method naturally capture all scattering mechanisms.^{41,42,81} The heat current was computed every ten time steps from the same atomic trajectories (positions and velocities) used for the VC-NMD and Gamma-NMD calculations. The thermal conductivity is determined from the maximum of the integral of the heat current autocorrelation function.