

## 2. From VC-ALD

should probably define this term much earlier

→ indicate that this approach does not consider the disorder explicitly

Assuming intrinsic and disorder scattering mechanisms to operate independently, the effective phonon lifetime can be found using <sup>the</sup> Matthiessen rule (cite), Ziman book?

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

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

Phonon-phonon scattering ( $\tau_{p-p}(\kappa)$ ) <sup>can be modelled</sup> is typically treated using anharmonic perturbation theory (ALD) including only three-phonon processes.<sup>4,11,35</sup> It has been demonstrated that

the effects of higher-order phonon processes become important at high temperatures.<sup>35,54</sup> In

<sup>we predict</sup> this work, the intrinsic phonon lifetimes  $\tau_{p-p}(\kappa)$  are predicted using the method described in<sup>35</sup>, with all classical expressions to remain consistent with the classical MD-based methods NMD and GK.

Using harmonic perturbation theory, Tamura derives a general expression for mass point defect scattering.<sup>1</sup> By considering the symmetry properties of the FCC lattices considered in this work (Section II C), <sup>this expression reduces to</sup> it can be shown that<sup>1</sup>

$$\frac{1}{\tau_{p-d}(\kappa)} = \frac{\pi}{2} \rho_2 \omega^2(\kappa) D(\omega), \quad (14)$$

where  $D(\omega)$  is the density of states (Section III A) and

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

Here,  $c^{\mu}$  <sup>and  $m^{\mu}$  are</sup> is the concentration,  $m^{\mu}$  <sup>and</sup> is the mass of the  $\mu$ -th species and  $\bar{m}^{\mu}$  is the average mass. Bond disorder can be accounted for using a similar expression with an average atomic radius or suitable scattering cross-section.<sup>26,27</sup> For the binary LJ argon and SW silicon alloys considered <sup>here</sup>, there is one atom type in the unit cell with  $\mu = i, j$ , so that the alloying atom labeled by  $m_{i-c}^i$  can be considered to be an "isotope" of <sup>the</sup> atom labeled  $m_c^j$ . This convention is

appropriate because isotopic impurities create perturbative disorder,<sup>1</sup> while we consider the use of Eq. (14) for large disorder. To calculate the disordered lifetimes  $\tau(\kappa)$  it is necessary, <sup>using Eqs. (14) and (15),</sup> to broaden the  $\delta$  function using a Lorentzian function.

The lifetimes predicted by VC-ALD for LJ argon at  $T = 10$  K and  $c = 0.05$  are shown <sup>a concentration of</sup> in Fig. 5(a). At low frequencies, where the density of states is Debye-like [ $D(\omega) \propto \omega^2$ , Fig.

Ref. 35  
Cite number

I don't understand this comment

Also plotted are the lifetimes for the perfect system and from the VC-ALD predictions at this concentration

you need one more sentence to justify you are at low T!

should already have defined this symbol earlier

Footnote to provide details from the VC-ALD predictions at this concentration

what  $\delta$  function

explain what is plotted, then  
disks

scales as

three

2],  $\tau_{p-p}(\kappa)$  follows a general scaling of  $\omega^{-2}$ , which is due to intrinsic 3-phonon scattering processes. (cite) From Figs. 4 and 5 (a), the scaling  $\tau \propto \omega^{-2}$  can be observed in the VC-NMD, <sup>is also</sup> Gamma-NMD and VC-ALD predicted results. Under the Debye approximation, the phonon scattering due to mass point-defects is given by  $A\omega^{-4}$ , <sup>predicted by Eq. 4 (b)</sup> where  $A$  is a constant related to the unit cell volume, branch averaged group velocity, and disorder coupling strength ( $g_2(b)$ , Eq. (15)). The frequency dependence ( $\omega^4$ ) is the same as Rayleigh scattering, which is valid at low frequency and <sup>is</sup> observed in both the NMD (Fig. 4) and ALD (Fig. 5 (a)) predicted lifetimes. <sup>in the mid-frequency range.</sup> VC-ALD does not predict the behavior of the lifetimes at high frequency, <sup>observed in VC-NMD</sup> for LJ argon, ~~constant~~. From Fig. 5 (c), the thermal conductivity frequency spectrum demonstrates that the <sup>thermal</sup> conductivities of LJ argon and its alloys are dominated by high frequency modes (Fig. 5 c). (cite) <sup>from this plot</sup> It can be seen that VC-ALD underpredicts the thermal conductivity at high-frequencies, <sup>consistent with</sup> precisely where the lifetimes are underpredicted by VC-ALD compared to VC-NMD.  $(\frac{\Delta m}{m} = -)$

The Tamura theory was developed to predict the reduction of lifetimes in isotopic Ge, which is only perturbatively disordered. The importance of  $n$ -order <sup>higher i.e.</sup> ( $n > 2$ ) interactions in the Tamura theory become important with increasing disorder strength  $g_n$  (Eq. (15)).<sup>1</sup> For isotopically-disordered Ge, the higher-order contributions were estimated to be negligible for at all frequencies.<sup>1</sup> For LJ argon and the large concentrations and mass ratios considered in this work, the terms higher order terms are order <sup>unity</sup> and larger at high frequencies. It is possible that <sup>the</sup> higher-order interactions in the Tamura theory are responsible for the discrepancy of the lifetimes predicted by VC-NMD and Gamma-NMD versus VC-ALD at high frequency.

need to  
compare to  
ga!

Fig 5 should appear before  
next section

## D. Diffusivities

Once the group velocities and lifetimes are predicted, these <sup>is</sup> can be used to predict the mode thermal diffusivity. For large disorder, only modes at low frequency have well-defined group velocities and lifetimes. At high frequencies, it is not possible to specify a ~~mode~~ group velocity and lifetime independently,<sup>25,55</sup> and the mode thermal diffusivity must be considered ~~to predict thermal conductivity~~.

In the classical harmonic limit, where the specific heat  $c_p(\nu) \approx (k_B/V)$ , a vibrational mode's contribution to thermal conductivity is determined by the ~~mode~~ <sup>is mode-independent</sup> thermal diffusivity. ~~For phonons, the thermal diffusivity is~~

search that  $D_{ph,n}(\nu) = v_{g,n}(\nu) \tau(\nu)$ , analogous to Eq. (2). (16)  
~~For VC-NMD and VC-ALD,  $v_{g,n}(\nu)$  is calculated from the VC dispersion (Section III B) so that any differences in thermal diffusivity come from the predicted lifetimes. The lower limit for phonon thermal diffusivity is  $D_{ph,n}(\nu) \approx 0$  since the group velocities can approach zero (e.g., for modes such as optical, and those near the Brillouin zone boundaries) (cite)~~

In a disordered system, modes can transport heat by harmonic coupling due to disorder in the Allen-Feldman (AF) theory of diffusons.<sup>22</sup> In the high-scatter (HS) limit, (cite) the AF diffusivity of each mode is

$$D_{AF,HS} = \frac{1}{3} v_s a,$$

what does this equation have to do with AF? (17)

which leads to the AF, HS limit prediction for thermal conductivity, Eq. (3). The physical interpretation <sup>of Eq. (17)</sup> is that all vibrational modes transport heat at the sound speed and scatter with a mean free path of the lattice spacing. As seen in Fig. 5, for LJ argon alloy <sup>(b) the</sup> at a concentration of 0.05, VC-NMD and VC-ALD predict <sup>from Eq. (16)</sup> a significant number of modes with  $D_{ph}(\nu) \leq D_{AF,HS}$ .

[This can lead to an underprediction of the total thermal conductivity (Section ).] <sup>needed here?</sup>

While the AF, HS model assumes a mode-independent thermal diffusivity, the AF theory is capable of predicting the mode-specific <sup>thermal</sup> diffusivities.<sup>7,7,25,56</sup> Since the AF theory is harmonic, mode <sup>the frequency approaches zero</sup> diffusivities typically diverge as  $\omega \rightarrow 0$  because the vibrations are long-wavelength plane waves that weakly scattered by the disorder.<sup>57,58</sup> The mode-specific thermal diffusivities for the LJ argon amorphous phase <sup>are shown in Fig. 6. Except at the highest frequencies, the thermal diffusivity of all modes can be modeled using a mode-independent diffusivity of approximately  $D_{AF,HS}$ . Also shown in Fig. 6 are the AF predicted thermal diffusivities for</sup>

the explicitly disordered LJ argon superlattice <sup>at</sup> ~~and  $c = 0.5$~~  <sup>alloy at a concentration of As expected, predictions</sup>. While the AF theory is divergent ~~in the low-frequency limit for lattices, the finite system size limits the thermal diffusivities of the lowest frequencies.~~ The thermal diffusivity of all modes in the explicitly disordered lattice supercell are larger than  $D_{AF,HS}$  except at the highest frequencies, where they tend to zero as in the amorphous phase. (cite) This result supports the plausible lower-bound of the VC predicted phonon thermal diffusivity <sup>to be</sup>  $D_{ph} \geq D_{AF,HS}$ .