E. Discussion

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.[50,59] The VC-predicted group velocities, particluarly for $v_g(\frac{\kappa}{\nu}) << v_s$ or $v_g(\frac{\kappa}{\nu}) \approx 0$, are an underprediction of the representative velocity scale ~~for~~ the thermal diffusivity of high-frequency modes in the disordered lattice ~~as calculated from Eq. .~~ This is ~~demonstrated~~ by considering the AF theory predicted mode thermal diffusivities, which are finite for the ~~heavily disordered~~ LJ alloy at a concentration of 0.5 ~~(Fig.)~~. ~~For phonons~~, the thermal diffusivity can be zero because of the VC predicted group velocities, ~~which is not consistent with~~ the AF theory predictions.

Predictions from model disordered systems demonstrate the existence of a plateau of the thermal diffusivity at high frequency, which is consistent with the minimum phonon mean-free path hyopthesis[63] used in most models of thermal transport in disordered materials.[26,64,65] The concept of a vibrational mean free path is only valid, however, for low-frequency propagating modes in disordered systems.[50] The more fundamental proprety is the vibrational mode lifetime[56] or thermal diffusivity.[7,8,25,50]

The VC-NMD and Gamma-NMD predict lifetimes ~~that~~ are generally larger than the IR limit for LJ argon and its alloys (see Fig. 4). VC-ALD predicts essentially monotonically decreasing lifetimes with increasing frequency for the LJ argon alloys [Fig. 5(a)]. Because VC-NMD and VC-ALD use the same values for $v_g(\frac{\kappa}{\nu})$, the phonon mode diffusivities will therefore be are underpredicted for VC-ALD compared to VC-NMD for the LJ argon alloys ~~with a significant number of lifetimes below the IR limit (see Fig.)~~. There are thus two underpredictions to consider when interpreting the thermal conductivity predictions in Section : (i) underprediction of the thermal diffusivity that results from using the VC group velocities for VC-NMD and VC-ALD, and (ii) the underprediction of the mode lifetimes for LJ argon alloys by the VC-ALD perturbative models.

IV. THERMAL CONDUCTIVITY PREDICTIONS

The thermal conductivities of the LJ systems can now be predicted from Eq. (1) using the vibrational mode properties predicted by the VC-NMD and VC-ALD methods. Given the discussion regarding the VC-predicted mode properties in Section III E, we also predict ther-

mal conductivity using the equilibrium MD-based GK method, which is a top-down ~~method~~ approach that does not make any approximations about the nature of the normal modes. Thermal conductivities predicted by the GK method naturally capture all scattering mechanisms.[32,66,67] The main challenge in the GK method is how to specify the ~~converged value of~~ the thermal conductivity from the integral of the heat current autocorrelation function, ~~which is determined by the maximum of this integral.~~ The heat current was computed every 10 time steps from the same atomic trajectories (positions and velocities) used for the VC-NMD and Gamma-NMD methods.

To predict a bulk thermal conductivity, ~~finite-size~~ extrapolation is used,

$$\frac{k(N_0)}{k_0} = 1 - \frac{c_0}{N_0}, \tag{19}$$

where c_0 is a constant, ~~k_0 is the extrapolated bulk thermal conductivity, and $k(N_0)$ is the size-dependent thermal conductivity.~~[13] For VC-NMD and VC-ALD, the validity of ~~the finite-size scaling~~ requires that the low-frequency modes ~~in the system~~ be dominated by phonon-phonon scattering (i.e., $\tau \propto \omega^{-2}$) and follow the Debye approximation with respect to the group velocity DOS.[13,14] For LJ argon alloys, this requirement is satisfied for modest system sizes (for $N_0 = 6$ to 12) so that both VC-NMD and VC-ALD predictions can be extrapolated to a bulk value. For SW silicon alloys, the thermal conductivity is dominated by low-frequency modes, so that large system sizes are needed to satsify the extrpaolation requirements and only GK and VC-ALD can be used ($N_0 \leq 42$ in the present study, similar to the converged system sizes in[41]). This highlights the efficiency of the VC-ALD method, which is necessary when computationally expensive DFT calculations are used (Section).[4,10,11,14,68,69]

Bulk thermal conductivity predictions ~~are made~~ for VC-NMD, VC-ALD, and GK are tabulated in Table I and plotted in Fig. 7. While agreement between the three methods is found for the perfect crystal, VC-NMD and VC-ALD underpredict the alloy thermal conductivities compared to GK. Also plotted is the high-scatter thermal conductivity prediction, k_{HS} [Eq. (3)]. The underprediction is modest for VC-NMD, 20% or less for all concentrations. In Section III D, we argued for the existence of a minimum mode thermal diffusivity, D_{HS}. As shown in Fig. , the diffusivities of many high-frequency modes in the LJ alloys, predicted by both VC-NMD and VC-ALD, fall below this limit. Based on this observation, we propose that any thermal diffusivity below the limit be set to D_{HS}. The results of this adjustment, referred to as VC-NMD* and VC-ALD*, are plotted in Fig. 7. The adjusted

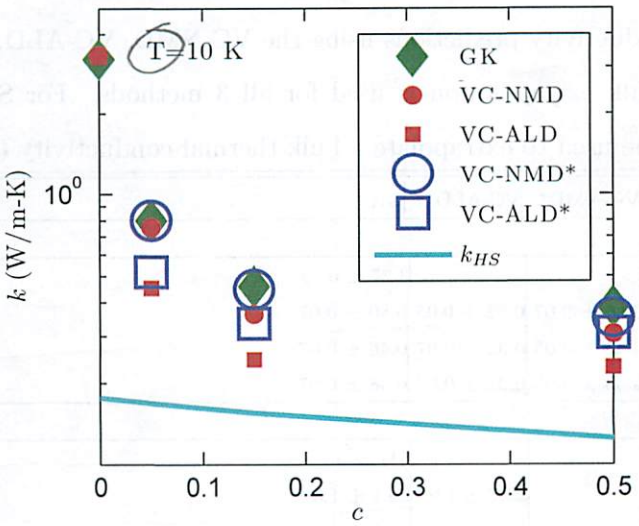

FIG. 7: Thermal conductivity predictions for LJ argon alloys at T=10 K using the VC-NMD, VC-ALD, and GK methods. The high-scatter thermal conductivity prediciton k_{HS} (see Eq. (3)) and the high-scatter adjusted VC-NMD∗ and VC-ALD∗ are also plotted. The adjusted VC-NMD∗ is brought into agreement with GK method predictions, while the correction VC-ALD∗ is only marginally changed.

thermal conductivities predicted by VC-NMD* are within 10% of GK for all concentrations. Combined with D_{HS}, the VC-NMD predicted thermal diffusivities are good representations for the explicitly disordered modes present in the MD simulation.

The VC-ALD method underpredicts the thermal conductivity of the LJ argon alloys, where the underprediction is worst for a concentration of 0.05, where k_{VC-ALD}/k_{GK} is 0.56. By applying the high-scatter limit adjustment VC-ALD*, the thermal conductivities are brought into marginally better agreement, worst for a concentration of 0.05, where k_{VC-ALD^*}/k_{GK} is 0.65. The VC-ALD method fails to accurately predict the high-frequency mode thermal diffusivities for LJ argon alloys, which can be seen in Fig. 5 (b). Since the group velocities are the same for VC-NMD and VC-ALD, the underprediction of the high-frequency thermal diffusivities, and hence thermal conductivity, is due to the underpediction of the high-frequency mode lifetimes [Fig. 5(a)]. Thus the adjustment VC-ALD* fails to bring VC-ALD into agreement with VC-NMD and GK.

TABLE I: Thermal conductivity predictions using the VC-NMD, VC-ALD, and GK method. For LJ argon alloys, the bulk extrapolation is used for all 3 methods. For SW silicon alloys, only VC-ALD and GK can be used to extrapolate a bulk thermal conductivity (see Section IV).

c	VC-NMD	VC-ALD	VC-NMD*	VC-ALD*	GK
LJ					
0.00	3.33 ± 0.12	3.45 ± 0.05			3.27 ± 0.09
0.05	0.76 ± 0.07	0.45 ± 0.05	0.80 ± 0.07	0.52 ± 0.05	0.80 ± 0.07
0.15	0.36 ± 0.04	0.24 ± 0.03	0.45 ± 0.05	0.33 ± 0.07	0.46 ± 0.07
0.50	0.31 ± 0.04	0.23 ± 0.03	0.35 ± 0.05	0.31 ± 0.07	0.38 ± 0.07
SW					
0.00		484 ± 21			517 ± 33
0.05		23.5 ± 1.9		23.7 ± 1.9	20.1 ± 1.5
0.15		11.9 ± 0.9		12.0 ± 0.9	9.90 ± 0.9
0.50		11.1 ± 0.9		11.2 ± 0.9	9.30 ± 0.9

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The failure of HC-HD to predict the thermal conductivities of the LJ alloys is due to an underprediction of the high-frequency mode lifetimes, which dominate the thermal conductivity [see Sections..., Figs...].

V. SW SILICON

To provide a contrast, where it is known that low frequency modes dominate the thermal conductivity.

~~Because of the discrepancies between the VC-NMD and VC-ALD predicted mode properties and thermal conductivities for the LJ argon alloys~~, we now predict the mode properties and thermal conductivity for SW silicon ~~alloys which are "stiffer" (larger phonon group velocities and lifetimes)~~. The lifetimes for a concentration of 0.5 predicted by VC-NMD and VC-ALD are plotted in Fig. 8(a). The VC-NMD predicted lifetimes are generally larger than the IR limit for SW silicon alloys, similar to VC-NMD predictions for the LJ argon alloys (Fig. 4). Unlike the LJ argon alloys, the VC-NMD and VC-ALD predicted lifetimes agree over most of the frequency spectrum, except at the highest frequencies, where VC-ALD underpredicts VC-NMD and falls below the IR limit. The high-frequency plateau of the VC-NMD predicted ~~mode~~ lifetimes for LJ argon (Fig. 4) is not seen for SW silicon.

~~As shown in Fig. 8(c), the thermal conductivity of SW silicon alloys is dominated by low-frequency modes.~~ As seen in Figs. 8(a) and 8(b), VC-NMD and VC-ALD both predict a significant number of modes with $D_{ph}(\kappa) < D_{HS}$ for ~~both the LJ argon and~~ SW silicon alloys, similar to the findings for the LJ alloys [Fig. 5(b)].

From p24 ⊛ For SW silicon, we can only make bulk thermal conductivity predictions for VC-ALD and GK (see Table I and Fig. 9) because computational demands limit the system sizes accesible with VC-NMD. ~~From Table I,~~ The thermal conductivities predicted for SW silicon alloys by VC-ALD and GK are in agreement within ~~less than~~ 20%, ~~even without the adjustment VC-ALD*~~, where VC-ALD ~~actually~~ overpredicts compared to GK. The predicted thermal conductivities for SW silicon alloys at all concentrations are over an order of magnitude larger than the ~~high-scatter~~ HS prediction k_{HS} [Eq. (3)]. Because thermal transport in SW silicon is dominated by low-frequency ~~dominant~~ modes, ~~however~~, the high-scatter adjustments ~~VC-NMD* and~~ VC-ALD* vary by only one percent compared to the unadjusted ~~VC-NMD and~~ VC-ALD.

~~For the large concentrations and mass ratios considered in this work, the terms higher order terms in the Tamura perturbation theory are order 1 and larger at high frequencies~~ As discussed in (see Section VI), it is possible that higher-order interactions in the Tamura theory are ~~also~~ responsible for the discrepancy of the lifetimes predicted by VC-NMD and VC-ALD in SW silicon at the highest frequencies, but this discrepancy is unimportant to the overall thermal transport. (I would end this section here)

The LJ argon and SW silicon alloys ~~studied in this work~~ have different ranges of phonon

nothing new here- needed?

frequencies, lifetimes, group velocities, and total thermal conductivity. For bulk silicon, the thermal conductivity is dominated by low-frequency modes,[5,11,30,31] which is also true for bulk and alloyed SW silicon (see Fig. 8). For SW silicon, VC-ALD predicts thermal conductivities in reasonable agreement with the explicitly disordered GK method (Fig. 9). For LJ argon, VC-ALD underpredicts the high-frequency phonon lifetimes and thermal diffusivities (see Fig. 5), leading to an underprediction of thermal conductivity when compared to VC-NMD and GK (see Section IV).

The results for the SW silicon and LJ argon alloys suggest that thermal modeling of ordered and disordered lattices can be separated into two broad groups: low-frequency dominated and full-spectrum materials. Materials dominated by low-frequency modes tend to have high thermal conductivities, which is due to their large group velocities and long lifetimes.[30,31,70,71] These low-frequency modes follow closely the scalings predicted by the perturbative VC-ALD models, which are valid at low-frequencies.

comment on HS

all of this is better suited to the summary

LJ argon is a material whose thermal transport has significant contribution from high-frequency modes, even for the bulk [see Fig. 5 (c)]. This high-frequency range is where we predict that the perturbative Tamura theory will have non-negligible contributions from higher-order interactions (see Section III C 2). While the higher-order interactions in the Tamura theory are also predicted to be non-negligible for SW silicon, this does not affect the thermal conductivty predictions signifcantly because high frequencies modes are unimportant to thermal transport. This is also true for the thermal conductivity spectrum of SiGe alloys from predictions[9,11,70] Experimental measurements[30,31,71] For example, the thermal conductivity of SiGe alloys exceeds the high-scatter limit by more than an order of magnitude at room temperature for all com- positions.[26,30,31]

Based on the thermal conductivity predictions for VC-NMD* and the well-defined peaks in the structure factors (Fig. 3), the reduction of group velocities in disordered lattices due to zone folding seems to be an underprediction of the group velocity of moderate to high frequency modes.[45]

VI. SUMMARY

~~The concept of simple alloying remains at the forefront of efforts to control or minimize the thermal conductivity of semiconducting and thermoeletric materials (cite SiGe nanoporous,~~

Summary needs organizational work.
I suggest=

1. Quick review of everything you did
2. General discussion of low-w vs. Full spectrum materials
3. Why VC-AlD is important
4. conditions under which VC-AlD (Tamura) will breakdown, effects on k prediction
5. Recommendations

Why not to repeat yourself- aim for one linear flow

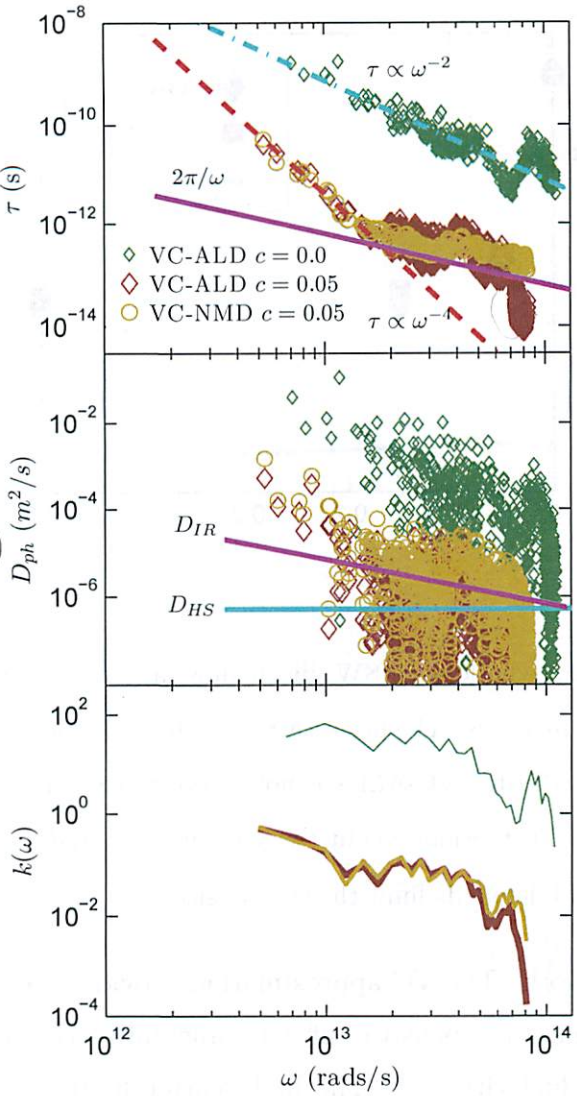

FIG. 8: (a) predicted lifetimes for VC modes using VC-NMD and VC-AlD for SW silicon. (b) predicted VC mode thermal diffusivities, compared to the AF,HS limit. (c) the thermal conducitivty frequency spectrum, which is peaked at low frequency, in contrast to LJ argon (Fig. 5).

~~PbTe)~~ Results in this work suggest that the lower limit for the vibrational mode thermal diffusivity in alloys is $(1/3)v_s a$.

The results in this work support the idea of a minimum thermal diffusivity for the vibrations in disordered lattices.(cite) Although this minimum thermal diffusivity is usually interpreted as a minimum mean free path, we find that concept is not necessary for inter-

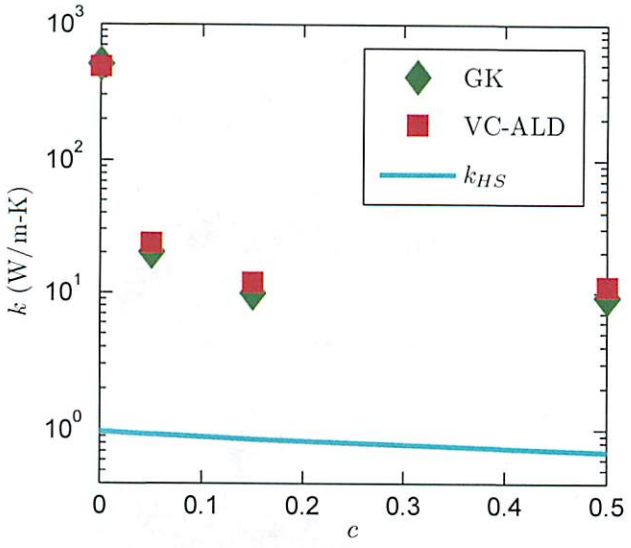

FIG. 9: Thermal conductivity predictions for SW silicon alloys at a temperature of 300 K using the VC-NMD, VC-ALD, and GK methods. The high-scatter thermal conductivity prediciton k_{HS} (see Eq. (3)) is also plotted. The adjusted VC-ALD* is not shown since it differs by only one percent compared to VC-ALD. The bulk thermal conductivity cannot be predicted using the VC-NMD method because computational demands limit the system sizes.

preting the results of this work. The VC approximation provides a computationally cheap framework, which is essential for expensive but experimentally accurate *ab initio* methods for predicting thermal conductivity.(cite) The high-scatter limit of thermal diffusivity is more useful for examing the thermal transport in alloys under the framework of the VC approximation. The fundamental quantity is the mode lifetimes and the group velocity is an approximation, and expressed together as thermal diffusivity they can be interpreted in the presence of disorder.

The VC approximation results in two underpredictions for modes at high frequencies: (i) underprediction of the disordered vibrational thermal diffusivities because of the VC predicted group velocities, and (ii) underprediction of the disordered mode lifetimes by the perturbative VC-ALD method. The validity of the VC approxiation has been verified for SW silicon alloys, which is a model system dominated by low-frequency modes. The underprediction of both the mode group velocities by the VC and the lifetimes by VC-ALD

occurs at the highest frequencies for SW silicon alloys, but these modes are unimportant to thermal transport. This is the plausible explanation for the success of the VC approximation phenomologically and predictively for low-frequency dominated, high thermal conductivity materials.(cite)

For LJ argon alloys, which have significant thermal transport from high-frequency modes, VC-NMD and VC-ALD both underpredcit the thermal conductivity compared to the system-level GK method. VC-NMD underpredicts only modestly, and can be brough into good agreement with GK by applying the high-scatter limit adjustment VD-NMD*. For VC-ALD, the high-scatter limit adjustment VC-ALD* still underpredicts compared to GK and VC-NMD*, suggesting that the perturbative Tamura theory is not appropriate for LJ argon alloys. This may be true for the high-frequency modes of any disordered lattice,(cite) and the high-scatter limit $D_{AF,HS}$ should be considered whenever the perturbative VC-ALD method is used.

Acknowledgments

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Appendix A: NMD using Non-Exact Normal Modes

For a normal mode of the lattice supercell used for the MD simulations, the autocorrelation of the total normal mode energy autocorrelations are damped exponentials with a decay time $\tau(^{\kappa}_{\nu})$ and the kinetic energy autocorrelation is a cosinusodial exponentially-damped oscillation with frequency $2\omega(^{\kappa}_{\nu})$.(cite AHRT) When using the VC normal modes to map the MD simulation trajectories from the explicitly disordered lattice supercells, the mode total and kinetic energy autocorrelation fucntions do not always follow the simple functional forms, see Fig. 10 (a) and (b). By calculating the phonon mode spectral energy Φ, which is a phonon mode energy method in the frequency-domain,[24] artifacts such as multiple peaks

are

~~in a given mode's energy spectrum Φ can be~~ observed for high concentrations, $c = 0.5$, Fig. 10 ~~(d)~~.

These artifacts ~~in the mode energy spectrum and autocorrelations~~ are not surprising given two considerations: (i) the MD simulations contain explicit disorder which influences the atomic trajectories, (ii) the VC normal modes are not the exact normal modes ~~and~~ of the explicitly disordered lattice supercells. ~~It is important to remember that the VC normal modes are exact in the limit $c \to 0$.~~

not relevant to your analysis

~~In the case of multiple peaks in the VC phonon mode spectrum Φ, the choice of which peak to fit to predict the phonon properties can be ambiguous.~~ An effective lifetime can be predicted ~~unambiguously~~ using Eq. (11) because the VC ~~phonon~~ total mode energy autocorrelations still decay to zero in a finite time ~~Fig. 10 (b)~~. This results is to be expected given that the atomic trajectories contain information about the lattice energy, which from general statistical physics principles will have exponential relaxation behavior in an equillibrium ensemble.[72–74]

↓ not totally satisfying