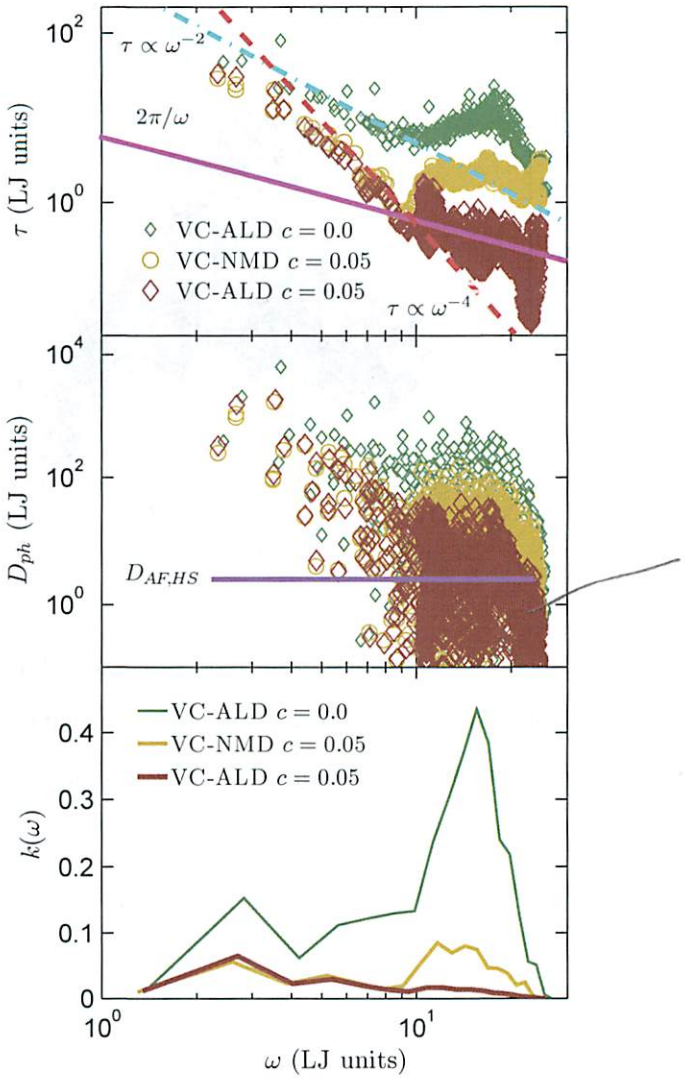
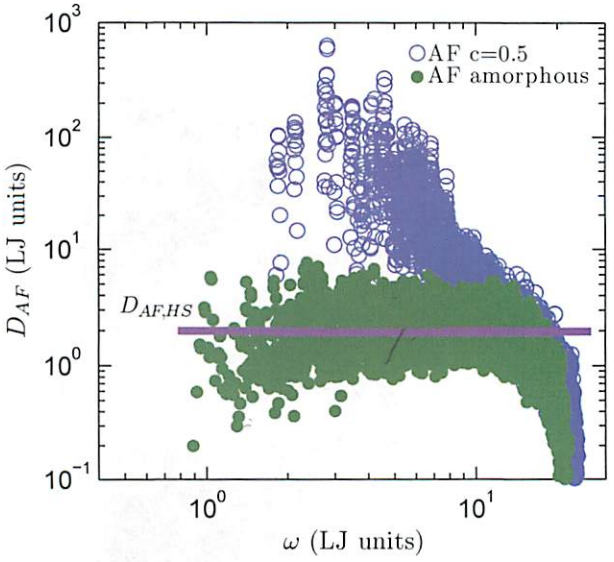


FIG. 5: (a) predicted lifetimes for VC modes using VC-NMD and VC-AlD for LJ argon ($T = 10$ K, $N_0 = 10$ and $c = 0.05$). (b) predicted VC mode thermal diffusivities, compared to the AF,HS limit. (c) the thermal conducitivty frequency spectrum, which is peaked at high frequency, in contrast to SW silicon (Fig 8).

Need a comment about VC-ALD vs. VC-NMD at $c=0$



IR equivalent ?

FIG. 6: AF theory predictions of disorded mode thermal diffusivities for LJ argon disorded lattice supercell and amorphous phase. The mode thermal diffusivities predicted for the disorded lattice supercell are all finite, except at the highest frequency where they tend to 0 as in the amorphous phase.

Do you need to discuss diffusivity in this section to make the two points?

how could $v_g \sim 0$ be an underprediction?

E. ~~Mode Properties~~ Discussion

For disordered systems, it is only possible to assign a unique lifetime and group velocity to vibrational mode~~s only~~ in the low-frequency, propagating limit.[25,55] ~~This implies that~~ the VC ~~predicted~~ group velocities, particularly for $v_g(\kappa_\nu) << v_s$ or $v_g(\kappa_\nu) \approx 0$, are an underprediction of ~~the~~ representative velocity scale for the thermal diffusivity of high-frequency modes in the disordered lattice. Predictions from model disordered systems demonstrate the existence of a plateau of the thermal diffusivity, which is consistent with the minimum phonon mean-free path hyopthesis.[59] ~~A minimum vibrational mean free path is~~ used in most models of thermal transport in disordered materials.[23,52,53] ~~However,~~ the concept of a vibrational mean free path is only valid for low-frequency propagating modes in disordered systems.[25] The more fundamental proprety is the vibrational mode lifetime[51] ~~and~~ thermal diffusivity.[7,8,22,25]

VC-NMD and Gamma-NMD predicts lifetimes ~~which~~ are generally larger than the IR limit for LJ argon (Fig. 4. VC-ALD predicts essentially monotonically decreasing lifetimes with increasing frequency for ~~both~~ LJ argon (Fig. 5 (a)). Because VC-NMD and VC-ALD use the same ~~predictions~~ for $v_g(\kappa_\nu)$, the phonon mode diffusivities ~~$D_{ph}(\kappa_\nu)$~~ are underpredicted for VC-ALD compared to VC-NMD for LJ argon alloys. There are thus 2 underpredictions to consider when ~~predicting~~ the thermal conductivities: underprediction of the thermal diffusivity ~~assuming the~~ VC group velocities for VC-NMD and VC-ALD, and the underprediction of the mode lifetimes for LJ argon alloys by the VC-ALD perturbative models.

IV. THERMAL CONDUCTIVITY PREDICTIONS

The thermal conductivity can now be predicted using the vibrational mode properties predicted by the VC-NMD and VC-ALD methods. Given the discussion of the VC-predicted mode properties in Section III E, ~~it is necessary to implement a third method for predicting~~ thermal conductivity. ~~We~~ choose the equilibirum MD-based ~~green-kubo (GK)~~ method(cite), which is a system-level method that does not ~~predict any mode-specific properties.~~ Thermal conductivities predicted by GK naturally capture ~~the effects of whatever~~ scattering meachanisms ~~are present in the MD simulation without any assumptions.~~[31,60,61] ~~For~~ GK, ~~the thermal conductivities are defined by~~ the converged value of the integral of the heat current autocorrelation function ~~for a given system size N_0.~~

quantify VC-ALD differences

describe the procedure here or in a footnote

between the three methods good agreement is found for the perfect crystal,

~~For LJ argon,~~ Bulk thermal conductivity predictions are made for VC-NMD, VC-ALD, and GK using a finite simulation size extrapolation procedure ~~(Section II C)~~ and are ~~shown~~ plotted in Fig. 7. ~~For LJ argon,~~ VC-NMD and VC-ALD underpredict the thermal conductivity of alloys compared to GK. The underprediction is ~~only~~ modest for VC-NMD, ~~on the order of~~ 20% or less for all concentrations. ~~Based on the limit $D_{AF,HS}$ (Eq. (17)), the thermal diffusivities predicted by Eq. (16) for VC-ALD and VC-NMD can be adjusted such that any mode with $D_{ph} < D_{AF,HS}$ is given $D_{ph} = D_{AF,HS}$.~~ The results of this adjustment, referred to as VC-NMD* and VC-ALD*, ~~is shown~~ are plotted in Fig. 7. The thermal conductivities predicted by VC-NMD* ~~is brought into agreement with~~ are within 10% of GK ~~by approximately 10% or less~~ for all concentrations. Combined with $D_{AF,HS}$, the VC-NMD predicted thermal diffusivities ~~seem to be fair~~ are good representations for the explicitly disordered modes present in the MD simulations.

The VC-ALD method underpredicts the thermal conductivity of LJ argon alloys, where the underprediction is worst for ~~the~~ concentration of 0.05, where k_{VC-ALD}/k_{GK} is 0.56 (error bars are on the order of the large symbol sizes in Fig. 7). By applying the high-scatter limit adjustment VC-ALD*, the thermal conductivities are brought into marginally better agreement, worst for a concentration of ~~c=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.

make this comment earlier

not Italic

→ more modes in VC-ALD are being corrected

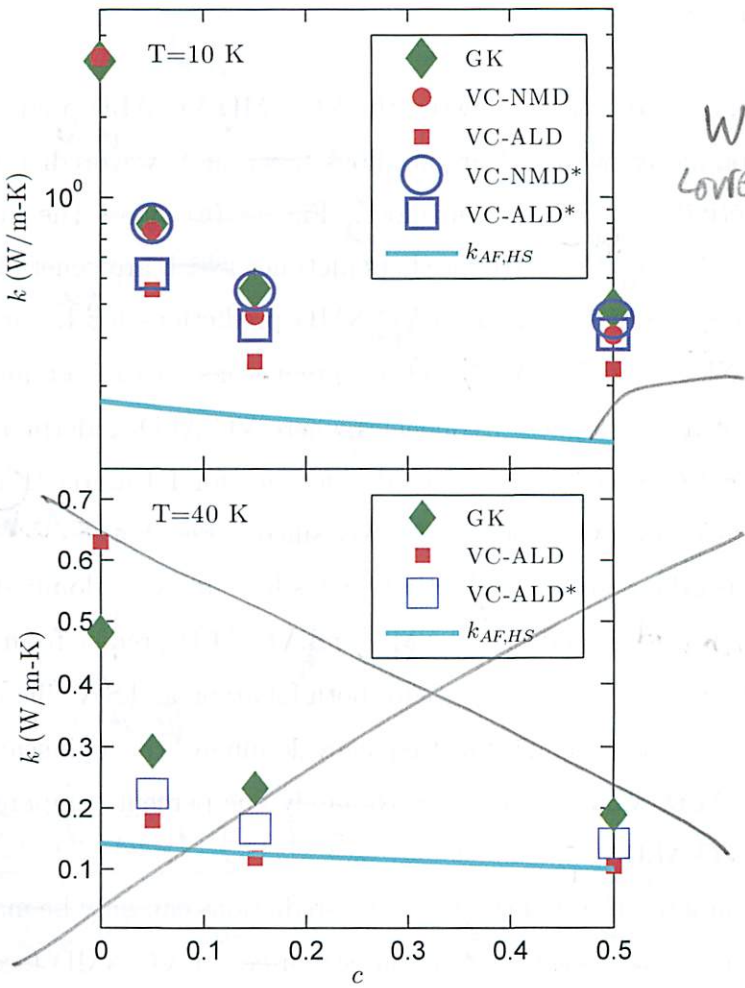
this discussion requires a quantification of uncertainty to provide context

In Section III D, we argued for the existence of a minimum mode thermal diffusivity, D_{HS}. As shown in Fig 5(b), 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}.

(A quick discussion of [24] Fig. 5(c) might be good here.)

discussion is not totally convincing / sufficient

I wonder if a table of this data would be better?



What about a correction based on IR?

you don't discuss this limit in the text

remove

FIG. 7: (a) thermal conductivity predictions for LJ argon alloys at T=10K using the VC-NMD, VC-ALD, and GK methods. (b) (getting rid of this) thermal conductivity predictions at T=40K

(too much to run NMD (no test))

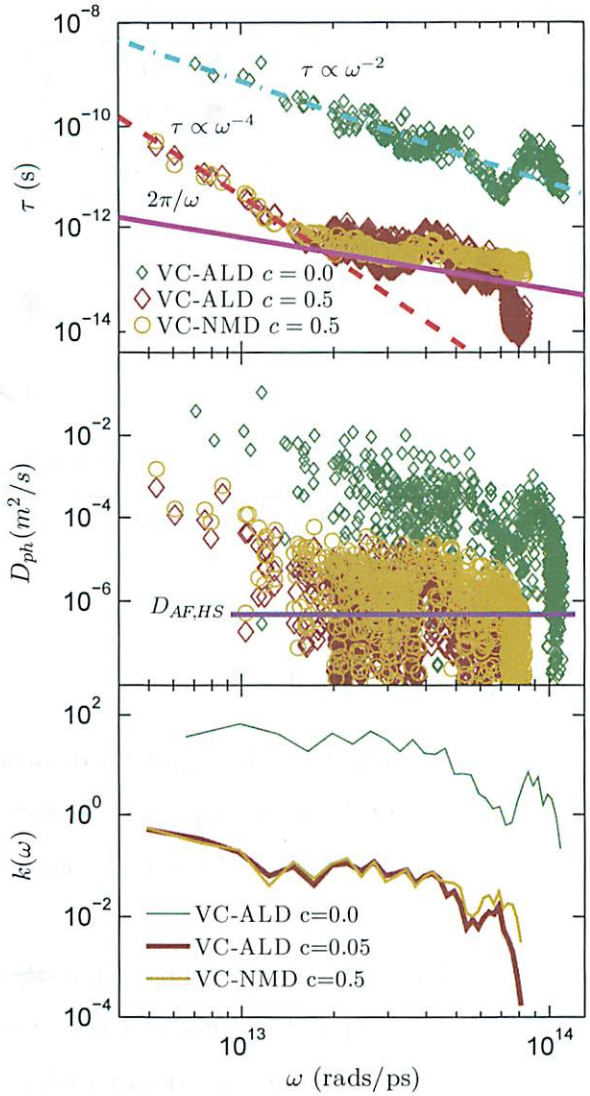
V. SW SILICON

Becasue of the discrepancies between the VC-NMD, VC-ALD predicted mode properties and thermal conductivities for LJ argon alloys ~~(Section)~~, we predict the mode properties and thermal conductivity for SW silicon alloys. ~~Fig. 8 (a) shows~~ The lifetimes predicted by VC-NMD and VC-ALD. VC-NMD predicts lifetimes ~~which~~ are generally larger than the IR limit for SW silicon alloys, similar to VC-NMD predictions for LJ argon (Fig.). Unlike LJ argon, VC-NMD and VC-ALD lifetime ~~predictions~~ agree over most of the frequency spectrum, except at the highest frequencies, where VC-ALD underpredicts. ~~While there is~~ a plateau of the VC-NMD predicted mode lifetimes for LJ argon (Fig.), ~~this plateau of lifetimes at high-frequency~~ is not seen for SW silicon ~~(Fig. 8 a)~~.

~~From~~ Fig. 8 (c), the thermal conductivity of SW silicon alloys is dominated by low-frequency modes. As seen in Fig. 5 and 8, VC-NMD and VC-ALD predict from ~~Eq. (16)~~ significant number of modes with $D_{ph}(\overset{\kappa}{\nu}) < D_{AF,HS}$ for both LJ argon and SW silicon. ~~However,~~ because thermal transport in SW silicon is low-frequency dominant, the high-scatter adjustments VC-NMD* and VC-ALD* vary by only ~~approximately~~ one percent compared to the unadjusted VC-NMD and VC-ALD.

For SW silicon, bulk thermal conductivity predictions ~~can only be made~~ for VC-ALD and GK (Fig. 9) because ~~of the~~ limited system size ~~used for~~ VC-NMD ~~(see Section)~~. For SW silicon, the thermal conductivities predicted by VC-ALD and GK are in better agreement, even without the adjustment VC-ALD*. VC-ALD actually overpredicts by roughly 20% for $c \geq 0.05$ compared to GK.

For LJ argon and the large concentrations and mass ratios considered in this work, the terms higher order terms are order 1 and larger at high frequencies. For SW silicon alloys the higher-order terms are also large, while good agreement is observed at all but the highest frequencies for VC-NMD and VC-ALD (Fig. 8 (a)). 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, but this discrepancy is unimportant to the overall thermal transport.



I think that you should be able to integrate sections IV, VI to make a good story.

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).

VI. THERMAL PROPERTIES DISCUSSION — not a great section title

The LJ argon and SW silicon alloys studied in this work have different ranges of phonon frequencies, lifetimes, group velocities and total thermal conductivity. For bulk silicon(cite), the thermal conductivity is dominated by low-frequency modes(cite), which is also true for bulk and alloyed SW silicon (Fig. 8).(cite) For SW silicon, VC-ALD predicts thermal

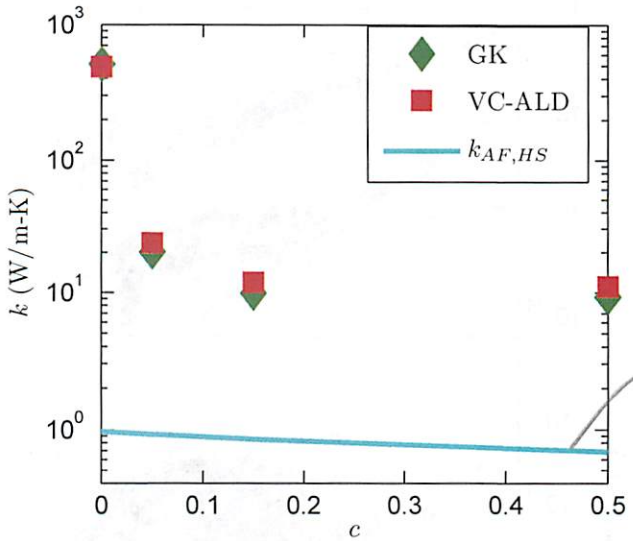


FIG. 9:

conductivities in reasonably ~~good~~ agreement with the explicitly disordered GK method (Fig. 9). For LJ argon, VC-ALD underpredicts the high-frequency phonon lifetimes and thermal diffusivities (Fig. 5), leading to an underprediction of thermal conductivity when compared to VC-NMD and GK (Section IV).

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

LJ argon is a material whose thermal transport has significant contribution from high-frequency modes, even for the bulk [Fig. 5 (c)]. This high-frequency range is where ~~the~~ perturbative Tamura theory is ~~predicted to~~ have non-negligible contributions from higher-order interactions (Section III C 2). While the high-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. ~~Even though VC-ALD underpredeits the mode lifetimes and thermal diffusivities at very~~ high frequencies ~~for SW silicon alloys (Fig. 8, these modes~~ are unimportant to thermal transport. This is also true for the thermal conductivity spectrum

experiments cannot measure the spectrum— your meaning is not clear

of SiGe alloys from first-princples predictions[11] and experimental measurements.[29,30,62,63] 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 ~~compositions~~ Garen Patton's.(cite)

what does this sentence mean?

The breakdown of the perturbative VC-ALD models for LJ argon is considering the thermal diffusivity of vibrational modes in the AF theory. A simple correction to the VC approximation can be made by considering a high-scatter limit for the mode specific thermal diffusivity (Section III D). This high-scatter limit is physically interpreted as vibrational modes propagating at the sound speed a distance of the lattice constant. However, the concept of a vibrational mean free path in a disordered system is only valid at low-frequencies.[25,55] For disordered vibrations, the lifetime and thermal diffusivity are the fundamental quantities.

repeating earlier text

For LJ argon, it is possible that the VC group velocities are an over-prediction for modes in a given interval of frequency, an effect which is compensated for by a ~~small~~ under-prediction of the lifetimes in the same interval of frequency when compared to Gamma-NMD (Fig. 4). The VC-NMD predicted mode lifetimes and thermal diffusivity adjusted VC-NMD*, predict thermal conducitivities in good agreement with the MD-based GK method. 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.[44]

some repitition here

VII. SUMMARY (did not read, awaiting next version)

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, 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 interpreting 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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