SPELLING!

Chapter 5

Conclusion

5.1 Overview and Contributions

5.1.1 Molecular Dynamics-based Methods for Predicting Vibrational Lifetimes

In Chapter 2, two MD-based methods for predicting phonon properties and thermal conductivity were compared. The Φ method, which is the NMD method in the frequency-domain, was properly derived starting with anharmonic lattice dynamics theory (see Appendix A.1). The meaning of the proposed spectral method, Φ', was clarified and related to the dynamic structure factor (see Appendix A.2). While the Φ' method does not accurately predict the mode lifetimes, the advantage of the Φ' versus the Φ method is that it does not require an eigenvalue solution for the mode eigenvectors. The dynamic structure factor, closely related to the Φ' method (see Appendix A.2), can predict frequency-dependent timescales from MD simulations for systems with a larger number of atoms than those studied in this work using the NMD method (see Section 5.2.2).

5.1.2 Thermal Transport in Alloys and the High-scatter Limit

In Chapter 3, thermal transport in two model alloys was investigated. The work provides several original insight into the physics of thermal transport in disordered lattices (i.e., isotopic solids and alloys). The first rigourous test of the virtual crystal (VC) approximation was presented. The VC-ALD technique has been used in a number of recent studies, [30, 32, 37, 38, 39] but its limits had not been assessed until this study. The limits of the VC-ALD approach were determined using computationally-inexpensive empirical potentials and self-consistently treating the disorder explicitly and as a perturbation. The results indicate that while VC-ALD is generally an accurate method for materials whose thermal conductivity is dominated by low-frequency vibrational modes, care must be taken when modeling alloys with low thermal conductivities, where significant underprediction of thermal conductivity is likely.

The high-scatter limit of thermal diffusivity, typically used in modeling amorphous materials, is directly relevant to the modeling of disordered lattices. Application of the VC approximation leads to vibrational mode diffusivities that are non-physical and the high-scatter limit provides a simple, physically-sound approach for correcting these predictions.

The following calculations that were performed are novel additions to the literature:

- Use of the VC-NMD method to model disordered lattices explicitly. This approach is limited in that the group velocity cannot be extracted so that thermal conductivity cannot be predicted. The novel contribution is the use of NMD to predict the lifetimes of a disordered lattice using VC-NMD, where the normal modes of the Virtual Crystal (VC) are used as an approximation (see Section 3.3.3.1 and Appendix A.4).

- To model the disorder explicitly, the AF Theory calcualtions were perfomred on a disodered lattice (Section 3.3.4). This theory has only previously been applied to amorphous phases. [48, 52, 62, 157] The AF theory predictions showed that the lower-limit of diffusivity of high-frequency modes in a disordered lattice is the high-scatter limit, in contrast to the VC-NMD ans VC-ALD methods, which incorrectly predict that the limiting value

is zero. Identification of this high-scatter limit of mode diffusivity was essential for identifying the breakdown in the VC methods. The high-scatter limit of diffusivity is usually assumed, without theoretical justification, in phenomological models for disordered and amorphous materials. [1, 2, 72] This study gives self-consistent justification for its use.

- Calcualtion of the structure factor of disordered lattices to predict group velocities (Section 3.3.2). The structure factor was calculated for modes in a model disordered lattice, which has previously been calculated for modes in amorphous materials. [48, 52, 73, 75, 152, 153, 169, 170, 173, 175, 177, 178, 180, 193, 194, 195, 196, 197] The structure factor predictions help to demonstrate that the VC-predicted group velocities are an underprediction of the representative velocity scale for mode diffusivities in the disordered lattice. While previous studies have attempted to predict the group velocity of modes in disordered systems, there is no theoretical justification for the methods used. [62, 84, 85, 102, 149, 151] The structure factor provides a rigorous manner to estimate group velocities and is a significant contribution to understanding how to predict the correct velocity scale for mode diffusivities in disordered systems. (but you didn't actually use these values)

By using all four methods discussed in Section 1.3, a self-consistent study of the VC approximation identified important connections between the modeling of disordered lattices and amorphous materials. By using three phases of LJ argon (perfect crystal, disordered lattice, and amorphous phase), the applicability of the different methods for predicting the thermal conductivity and mode-properties was demonstrated:

- MD-based GK method: suitable for modeling all three phases, but does not predict the mode properties.
- Phonon-based VC-ALD and VC-NMD: suitable for the perfect crystal and disordered lattices with the high-scatter limit correction.
- The AF theory of diffusons: suitable for the high-frequency modes of the disordered lattice and all modes of the amorphous phase.

(for LJ)

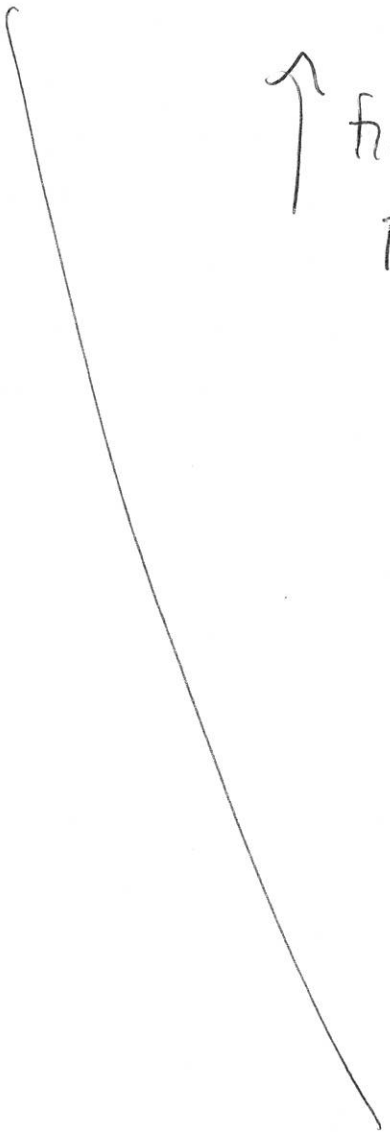
5.1.3 Mean Free Paths of Propagating Modes in Disordered Materials

In Chapter 4, a clear theoretical and modeling framework for amorphous materials was presented, which can form the basis for studying a range of disordered materials. This modeling framework grew as a natural extension of the work and results from Chapter 3. The NMD-predicted lifetimes, along with the material's sound speed, can be used with the AF theory diffusivities to determine the transition from propagating to non-propagating modes (Section). The challenge is that in disordered materials, the group velocities are not well-defined and there is no theoretical basis to predict them.[62, 84, 85, 102, 149, 151] Instead, the mode diffusivities are the fundamental quantities, and the predictions from both the NMD and AF theory methods must be considered simultaneously.

The following calculations that were performed are novel additions to the literature:

- Identified the effects of metastability in amorphous materials on predicting lifetimes using the NMD method (see Section 4.3.1 and Appendix A.5). Metastability is likely to affect the application of the NMD method in other ordered and disordered systems with weak atomic bonding (see Section 5.2.1).
- Identified differnces in the structural properties of a-SiO_2 and a-Si that lead to a substantial difference in the propagating contributions to thermal conductivity in each.
- Predicted the effective dispersion from the static structure factor to estimate mode group velocities (Section 4.4.2). While effective dispersions have been predicted from the structure factors for models amorphous materials previously, they had not been used to help predict the thermal conductivity. The effective dispersions justify the use of the sound speed at low frequencies.
- Using the justified sound speeds, it was demonstrated that the NMD-predicted diffusivities are more reliable than those predicted by the AF theory at low frequencies (Section 4.4.5).
- By comparing predictions from the NMD, AF, and GK method, it was demonstrated that an

ω^{-2} scaling of the low-frequency mode lifetimes best describes the model of bulk amorphous silicon (Section 4.5.1). Comparisons of the predicted thermal conductivity accumulations with experimental measurements demonstrates that the low-frequency scaling of the mode lifetimes is still under debate in the literature and further experimentation is necessary.



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5.1.4 Predictive ability versus Computational Cost

With the results from all of the studies presented in this work, a new ranking of the predictive capabilities for the four methods discussed in Section 1.3 is made in Table 5.1.

The GK method played an important role in verifying the mode properties predicted by all methods. In Chapter 2, the GK method provided a common comparison for the Φ and Φ' methods, which helps to confirm the disagreement between the two methods. In Chapter 3, the GK method provides a comparison for predictions from the VC-NMD and VC-ALD methods, which helps to identify the validity of the high-scatter limit of the diffuson mode diffusivities in disordered lattices. Finally, in Chapter 4, the GK method helps to confirm the scaling of the low-frequency contribution of the finite models of a-Si (Section 4.5.1). The GK method will ~~likely~~ be a valuable modeling tool for future work on disordered systems.

The VC-ALD method was shown to be limited to low frequency modes and best suited to high-thermal conductivity materials (Chapter 3). High thermal conductivity materials are typically dominated by the contribution from low-frequency modes that are well-modeled by VC-ALD. VC-ALD may not be well-suited for low thermal conductivity (full spectrum) materials, where the perturbation theory is not valid (Section 3). The AF theory models accurately the mid- and high-frequency modes in disordered materials (Section 3.3.4), but it does not properly model the low-frequency modes for disordered lattices. It also does not definitively model the low-frequency modes in amorphous materials (Section 4.4.5).

The VC-ALD method and AF theory can be supplemented by predictions from the NMD method, but additional assumptions are also required. The VC-NMD method is able to accurately predict the lifetimes of all vibrons in disordered lattices (see Section 3.3.3.1). However, the effective group velocities are still assumed to be those of the VC, which limits the NMD method's predictive ability (Section 3.4). Propagating modes in a-Si can be identified definitively by NMD-predicted lifetimes (see Section 4.4.4), but an assumption about the effective mode group velocities must be made (Section 4.4.5). Clearly, predicting group velocities for modes in disordered

Table 5.1: Ranking of the predictive ability of theoretical techniques for mode-level and system-level thermal properties for disordered systems.

System-level	CH Theory	ALD	AF Theory	NMD	GK
Mode-level	CH Theory	GK	AF Theory	ALD	NMD

materials is a major challenge that deserves further investigation. [62, 84, 85, 102, 149, 151]

With these findings, the predictive methods are re-ranked in order of their capabilities in Table 5.1. The NMD method, while the most computationally demanding of the four predictive methods (Table 1.1), is ranked first in mode- and second in system-level predictive capability. The reasons for these rankings are:

- The NMD method is derived correctly from anharmonic lattice dynamics theory. The NMD method (Φ) accurately predicts the mode lifetimes and thermal conductivities compared to the Φ' method.
- The VC-NMD method accurately predicts the mode lifetimes for disordered lattices compared to the VC-ALD method. This leads to better agreement with the GK method, which is the most accurate system-level method.
- The NMD method accurately predicts the low-frequency lifetimes for a-Si, while the AF theory predictions have large fluctuations that depend on the broadening factor. The scaling from the NMD lifetimes is used to extrapolate a bulk thermal conductivity which is in good agreement with the system-level GK method.

The ALD and AF theory are considered to be equivalent at predicting mode-level and system-level properties because, for disordered lattices, the VC-ALD method fails to accurately predict the mode lifetimes for high frequencies, while the AF theory is not valid for low frequencies. Either method could be considered superior depending on whether the material being studied is a disordered lattice that is low-frequency dominated or full-spectrum. The AF theory is superior if the material is amorphous, although there have been ALD predictions[207] of the mode lifetimes in a-Si that are in good agreement with NMD predictions[96, 97] in the literature.

5.2 Future Work

5.2.1 Large Unit Cell Materials

Large unit cell (LUC) materials are an important class of crystalline materials with a wide range of thermal transport applications [82, 87, 210, 211, 212]. LUCs have an ordered (crystalline) structure, but the unit cell of the crystal has a large number of distinct atoms. LUCs are effectively disordered over length scales on the order of the atomic spacing and their thermal conductivities can be as low as a glass [213]. One key advantage of LUC materials is that they are still ordered from the standpoint of electrons, that results in good thermoelectric performance [214, 215, 216].

Some LUC materials, such as SiO_2-based zeolites, have been well-studied.[82] Others, such as C_{60}[217] or PCBM, are currently being investigated for their thermal properties. [11] While experimental measurements of PCBM demonstrates that propagating modes contribute negligibly (see Fig. 5.1), the mechanisms for its *exceptionally-low* conductivity are still not understood. Modeling could provide the necessary insights.

From a modeling perspective, LUC materials pose a number of challenges, theoretically and computationally, as compared to small unit cell (SUC) materials:

- Predicting model-level properties using ALD is challenging because the computational time scales as n^4 (see Section 1.4).
- LUC are crystalline, but are often organic or organic/inorganic hybrid materials. The structure of LUC materials is often poly- or quasi-crystalline, with less long-range order than SUC materials. [212, 218]
- The presence of weak bonding in organic/inorganic materials [212, 219, 220] can lead to metastability (see Appendix A.5), which makes it challenging to perform the NMD method.

- MD simulations of LUC materials also face challenges. Based on the classical MD simulations of disordered materials studied in this work, systems sizes of 100-1000 atoms and simulation times of up to 1 ns are expected to be necessary to accurately predict thermal conductivity. DFT calculations are too computationally expensive for such MD simulations [29, 36, 107, 108, 109, 110, 221]. Because many LUC materials have complex bonding environments, even empirical interatomic potentials are often computationally-expensive. [222, 223, 224, 225]

tighten up

Based on the results in this work, there are several modeling strategies that can be used to study LUC materials:

- Identify signs of propagating modes from experimental measurements, if available. [11, 226]
- Based on the results for alloys (see Section 3.3.4), the AF diffuson theory may have application for LUC materials, particularly at high frequencies and for those LUC materials which are only quasi-crystalline, such as C_{60}.[218]
- The high-scatter limit for thermal conductivity (Eq. (3.3)) can be used to establish a plausible lower-bound for LUC materials.[213] Similarly, the high-scatter limit for mode diffusivity can establish lower-bounds on the mode-level properties.
- Perform calculations using computationally-inexpensive classical interatomic potentials to asses if DFT calculations are necessary.

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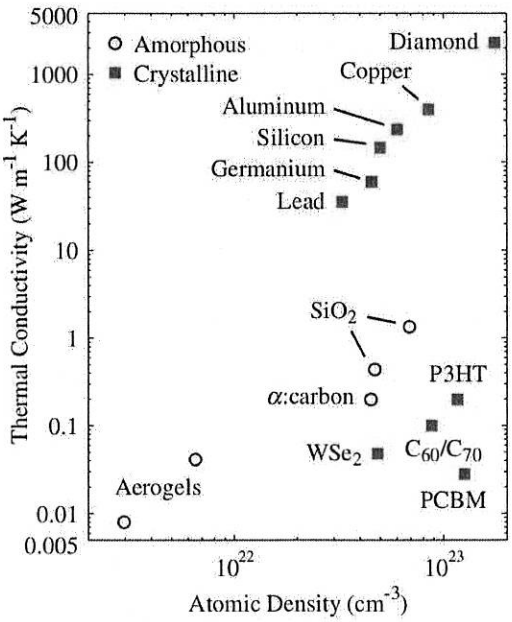

Figure 5.1: Range of thermal conductivity for crystalline, amorphous and LUC materials. Recent measurements on LUC materials show thermal conductivities much lower than bulk amorphous materials. Reproduced from Ref. 11.

not a great title- lifetimes?

5.2.2 Timescales from Larger MD Simulations

5.2.2.1 Exact Normal Modes

The NMD method used throughout this work is limited by its computational demands, which require a larger number ($\sim$ 100) of parallel processors to perform the analysis in a reasonable amount of time (less than 24 hours, see Appendix B.2.4.3). While the NMD method is trivially-parallelizable over the normal modes, the eigenvalue solution of the normal modes themselves is more computationally demanding. The eigenvalue solutions can be performed in parallel using the suggestions given in Section 5.2.3.

2.

A previous studied investigated the vibrational normal modes which has been used in a previous study on LJ argon to compute a small subset of the normal modes for a system of 32,000 atoms [206] using the Lanczos algorithm.[227] The same 32,000 system was subsequently studied using MD simulations and the dynamic structure factor,[171] which was discussed in Appendix A.2. While parallel eigenvalue solution can increase the system sizes accessible with NMD, the method is ultimately limited by the poor scaling of the run time and memory requirements (see Section 1.4).

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5.2.2.2 Dynamic Structure Factor

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MD simulations are computationally efficient. Systems sizes of nearly 10^6 atoms have been studied in this work, which were bulk systems with equal simulation side lengths in all three spatial dimensions. The dynamic structure factor, described in Section A.2, can predict vibrational timescales and does not need the eigenvectors of the exact normal modes to perform the mapping of the atomic trajectories. This method, combined with appropriately shaped supercells, could probe the timescales of vibrational modes up to wavelengths between 24 and 100 nm using similar computational resources to those used in this work. This presents an oppurtunity to compare with recent experimental measurements of spectral linewidths in the frequency ~~range~~ below 1 THz, which have been recently reported for a-SiO_2 [58, 59, 61, 228] but are lacking for

a-Si [57]. The current correlation function, closely related to the dynamic structure factor [173], can even be used to study the spectral character of motions in a fluid [229].

5.2.3 Comprehensive Package for Thermal Transport Calculations

Four different predictive methods were used in this work (see Section 1.3). ~~There~~ exist packages for performing some of the calculations necessary for these methods. However, no one package can perform all calculations necessary, particularly both the mode-level and system-level thermal transport properties. LAMMPS, for example, contains both the GK and direct methods for predicting the system-level thermal conductivity. A package to predict the mode-level properties is needed. Ideally, the mode-level properties could be predicted alongside the system-level calculations, as is necessary to perform the NMD and spectral techniques described in Section 2.2.1.

The Python language is an ideal environment for "gluing" together the availble codes, and extending their functionality in dynamic ways. For example, while the NMD method is trivially-parallelizable over the normal modes, the eigenvalue solution of the normal modes themselves is more computationally demanding. Standard routines for eigenvalue solutions of the dynamical matrix can calculate the exact normal modes for systems up to 8000 atoms in less than 24 hours using current computational resources. [134] These eigenvalue solution routines typically run on single processors. The eigenvalue solutions can be performed using the Portable, Extensible Toolkit for Scientific Computation (PETSc), which has routines for performing eigenvalue solutions in parallel. The PETSc pacakge has Python bindings contained in the petsc4py pacakage, which allows for easy interface the existing lattice dynamics package GULP[134] and MD package LAMMPS. [136] LAMMPS already contains a Python interface, and such an interface could be created for GULP using the f2py package.