

# Chapter 5

## Conclusion

### 5.1 Overview and Contributions

#### 5.1.1 Molecular Dynamics-based Methods for Predicting Lifetimes

In Chapter 2, two MD-based methods for predicting phonon properties and thermal conductivity were compared. The  $\Phi$  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,  $\Phi'$ , was clarified and related to the dynamic structure factor (see Appendix A.2). While the  $\Phi'$  method does not accurately predict the mode lifetimes, the advantage of the  $\Phi'$  versus the  $\Phi$  method is that it does not require an eigenvalue solution for the mode eigenvectors. The dynamic structure factor, closely related to the  $\Phi'$  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 rigorous 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 following calculations that were performed are novel additions to the literature:

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- Use of the VC-NMD method to model disordered lattices explicitly. The novel contribution is the use of NMD to predict the lifetimes of a disordered lattice using the normal modes of the Virtual Crystal (VC), ~~which is an approximation~~ (see Section 3.3.3.1 and Appendix A.3).
  - To model the disorder explicitly, the AF Theory calculations were performed on a disordered 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 and 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 phenomenological models for disordered and amorphous materials [1, 2, 72]. This study gives self-consistent justification for its use.
  - Calculation of the structure factor of disordered lattices to predict effective dispersion (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 struc-

ture 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].

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 of LJ argon (Section 3.3.1).

### → 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 4.4.5). 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.4). 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 differences in the structural properties of a-SiO<sub>2</sub> 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 methods, it was demonstrated that an  $\omega^{-2}$  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 demonstrate that the low-frequency scaling of the mode lifetimes is still under debate in the literature and further experimentation is necessary to resolve the .

#### 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  $\Phi$  and  $\Phi'$  methods, which helped to confirm the disagreement between the two methods. In Chapter 3, the GK method provided a comparison for predictions from the VC-NMD and VC-ALD methods, which helped to identify the validity of the high-scatter limit of the diffuson mode diffusivities in disordered lattices. Finally, in Chapter 4, the GK method helped to confirm the scaling of the low-frequency contribution of the finite models of a-Si (Section 4.5.1). The GK method will 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 (~~Chapter 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 (~~and~~ 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 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:

Table 5.1: Ranking of the predictive ability from low to high (left to right) 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

- (1)
- • The NMD method is derived correctly from anharmonic lattice dynamics theory ~~The~~ and
- • NMD method ( $\Phi$ ) accurately predicts the mode lifetimes and thermal conductivities compared to the  $\Phi'$  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, which results in good thermoelectric performance [214, 215, 216].

Some LUC materials, such as SiO<sub>2</sub>-based zeolites, have been well-studied [82]. Others, such

as C<sub>60</sub> [217] or PCBM, are currently being investigated for their thermal properties [11]. While experimental measurements of PCBM demonstrates that propagating modes contribute negligibly, 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.4), which makes it challenging to perform the NMD method.
- MD simulations of LUC materials also face challenges. While many LUC materials have complex bonding environments, DFT calculations are too computationally expensive to

perform MD simulations to predict thermal properties [29, 36, 107, 108, 109, 110, 221].

Even empirical interatomic potentials are often computationally-expensive because of the complex bonding terms required [222, 223, 224, 225].

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 (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<sub>60</sub> [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 assess if DFT calculations are necessary.

### 5.2.2 Lifetimes 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). 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.

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). Additional computational cost can be saved by computing only a small subset of the normal modes for a system. A previous study used the Lanczos algorithm[227] to compute a small subset of the normal modes for a 32,000 atom system[206]. The same 32,000 system was subsequently studied using MD simulations and the dynamic structure factor[171], which is discussed in the next section.

### 5.2.2.2 Dynamic Structure Factor

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 opportunity → to compare with recent experimental measurements of spectral linewidths at frequencies below 1 THz, which have been recently reported for a-SiO<sub>2</sub> [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). Packages exist 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 proper-

ties 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 available 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 package has Python bindings contained in the petsc4py package, which allows for easy interface with 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.

Inserting Eq. (A.24) into the right hand side of Eq. (A.23) gives

$$\begin{aligned} \sum_{\alpha}^3 \sum_b^n m_b \left| \sum_l^N \int_{-\infty}^{\infty} \dot{u}_{\alpha}(l_b; t) \exp[i\kappa \cdot \mathbf{r}_0(l_0) - i\omega t] dt \right|^2 = \\ \sum_{\alpha}^3 \sum_b^n \left| \frac{m_b^{3/2}}{\sqrt{N}} \sum_l^N \sum_{\nu}^{3n} D(\nu \alpha \cdot l_b) \exp[i\kappa \cdot \mathbf{r}_0(l_0)] \delta[\omega_0(\nu) - \omega] \right|^2, \end{aligned} \quad (\text{A.25})$$

where  $D(\nu \alpha \cdot l_b) = i\sqrt{2\pi}\omega_0(\nu) C_1(\nu) e^*(\nu \alpha \cdot l_b)$ ,  $\delta$  is the Dirac function, and values of  $\omega \leq 0$  are ignored. Thus, at zero temperature Eq. (2.8) is a superposition of Dirac functions at the phonon frequencies  $\omega_0(\nu)$ .

Equation (2.8) is similar to the definition of the displacement structure factor [152, 153, 173, 177, 194]

$$S_D(\kappa, \omega) = \frac{1}{4\pi\tau_0} \left| \sum_{\alpha}^3 \sum_b^n \frac{m_b}{N} \sum_l^N \int_0^{\tau_0} \dot{u}_{\alpha}(l_b; t) \exp[i\Theta] dt \right|^2, \quad (\text{A.26})$$

which is related to the static structure factor [48, 52, 73, 75, 152, 169, 175, 178, 180, 193, 195, 196, 197] (see Sections 3.3.2 and 4.4.2). [152]. The difference between Eqs. (2.8) and (A.26) is that the summations over  $\alpha$  and  $b$  occur inside the square modulus for Eq. (A.26). With the summations inside the square modulus, the orthonormality of the mode eigenvectors can be used to show that the static and dynamic structure factors are equivalent under the harmonic approximation. [152]

### A.3 NMD using Non-Exact Normal Modes

In Chapter 2, it was shown how NMD is applied to a perfect crystal. In reality, any crystal will have some deviation from perfect periodicity, which may be caused by a point defect, a dislocation, a grain boundary, or a free surface. In extreme cases, these deviations from periodicity will lead to the emergence of modified normal modes. For small perturbations, however, it is reason-

able to assume that the frequencies and mode shapes of the normal modes will be unchanged and that the effect of the perturbation will be on the lifetimes. Under this assumption, one can still project the atomic positions and velocities onto the normal modes of the unperturbed system.

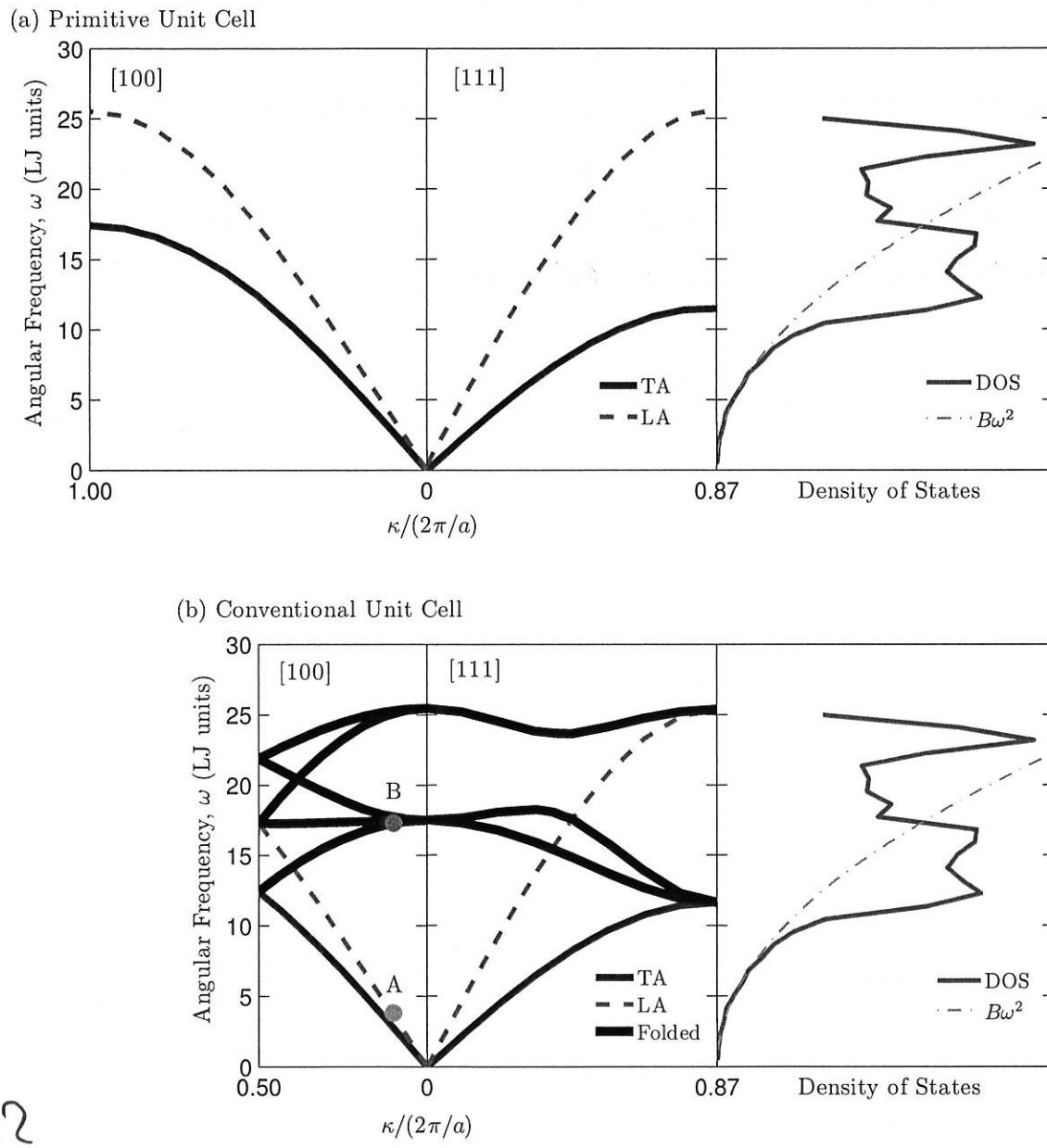
While one could perform the NMD by projecting the atomic positions and velocities onto the modes of the unperturbed system, it is more appropriate to use the virtual crystal approximation (see Chapter A, Section 3.3.3.1). Under the virtual crystal approximation, the system is replaced by one where all atoms have the same mass, equal to the average of the atomic masses in the system of interest. This system will have the same mode shapes as the original system, but the frequencies are modified due to the change in the average atomic mass.

Results for the time- and frequency domain approaches to NMD are shown for two modes for crystalline and alloyed LJ argon in Figs. A.2(a)-(d). These two modes are equivalent to those shown in the perfect crystal in Figs. A.1(b), 2.1(a), and 2.1(b). For a concentration,  $c$ , of 0.05, both peaks in the frequency domain are well-formed and a lifetime can be extracted by fitting the data to a Lorentzian function. This behavior is typical of all modes at a concentration of 0.05. The downward frequency shift is related to the increased average atomic mass.

For an alloy concentration of 0.5, the lower frequency mode still has a well-formed peak. The higher-frequency mode does not, however, such that a lifetime cannot be extracted by fitting to a Lorentzian function. Such behavior is typical of the higher frequency modes at high alloy concentrations. This change in behavior is also seen in the time domain, where the decay of the autocorrelation of the total mode energy is no longer a smooth exponential function. This behavior indicates that the virtual crystal normal mode is not a good description of the true normal mode. Equation (2.7) can be used to approximate a lifetime, as shown in Figs. A.2(c) and A.2(d).

These artifacts observed using NMD method with the virtual crystal approximation are not surprising given two considerations: (i) the MD simulations contain explicit disorder that influences the atomic trajectories, and (ii) the VC-normal modes are not the exact normal modes of the explicitly-disordered lattice supercells. An effective lifetime can be predicted using Eq. (2.7)

because the VC total mode energy autocorrelations still decay to zero in a finite time. This result 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 equilibrium ensemble. [18, 232, 233] The lifetimes predicted from the VC-NMD method are in reasonable agreement with those predicted from the Gamma-NMD method, which uses the exact normal modes of the disordered supercell (see Section 3.3.3.1).



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Figure A.1: Dispersion curves and full Brillouin zone density of states for a LJ crystal at a temperature of 10 K. (a) [100] and [111] dispersion curves and density of states based on the primitive (i.e., one atom) unit cell. (b) [100] and [111] dispersion curves and density of states based on the conventional (i.e., four atom) unit cell. The harmonic lattice dynamics calculations are performed using a resolution of sixteen wave vectors along the reciprocal lattice vectors of the conventional unit cell. The red and blue dots in (b) are the modes considered in Fig. 2.1.

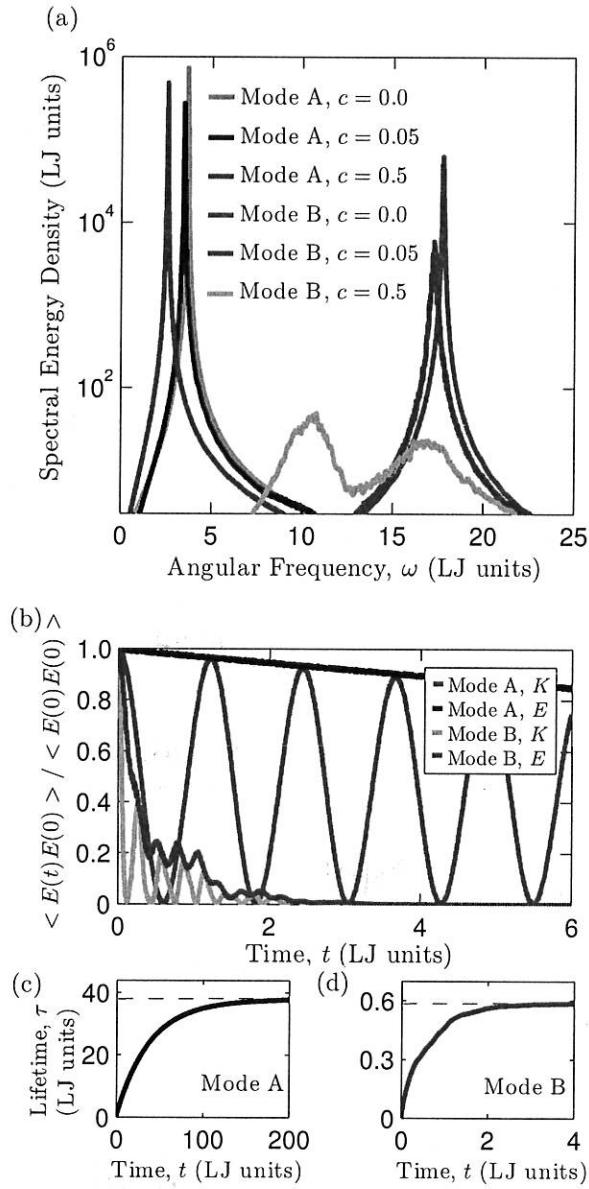


Figure A.2: Virtual crystal (a) frequency-domain and (b) time-domain NMD analysis for two modes in LJ alloys with concentrations of 0.05 and 0.5. For modes that are not well-approximated by the virtual crystal modes, the lifetime can be approximated using Eq. (2.7), as shown in (d).

## A.4 Effect of Metastability for Amorphous Solids on Normal Mode Decomposition

Amorphous materials may have many different atomic configurations with nearly equivalent po-

- tential energies, leading to potential metastability during MD simulations [52, 62, 187, 188, 189] •  
This meta-stability can cause errors when predicting vibrational lifetimes using NMD, which is demonstrated below.

This case study is performed on an amorphous LJ system with 2048 atoms at a temperature of 5 K. The amorphous solid is generated by liquefying the crystal, instantaneously removing all

- kinetic energy, and then relaxing the structure (i.e., a melt-quench, ~~see~~ Sections 4.3 and 4.3.1).
- The MD simulation parameters are the same as for the LJ crystal and alloy (~~see~~ Section 4.3). The LJ amorphous phase is metastable at this temperature and intermittently moves between very similar low-energy states. Evidence for the metastability can be found by analyzing the time-histories of the atomic displacements. As such, ~~normal mode decomposition~~, which requires the average atomic positions, will be an approximation.

- The time- and frequency-domain approaches to ~~normal mode decomposition~~ <sup>NMD</sup> are shown for two mode in the amorphous system in Figs. A.3(a) and A.3(b). Because the analysis is performed at the Gamma-point, the peaks are well formed, but they are not Lorentzian. We believe that the oscillations in the total energy correlation for the low frequency mode is a consequence of the metastability of the amorphous phase. As such, we extract the lifetimes by using Eq.(2.7), as shown in the inset to Fig. A.3(b). The lifetimes for the amorphous system are plotted in Fig. A.4. Compared to the crystal, the lifetimes show little frequency dependence and a significant number at low frequencies fall below the IR limit [Eq. (3.12)]. This <sup>result</sup> seems to be a consequence of the metastability, since this behavior is not observed for the NMD-predicted lifetimes for a-SiO<sub>2</sub> and a-Si (Fig. 4.4, Section 4.4.4), which were both annealed carefully to remove metastability (~~see~~ Section 4.3.1).

→ can't anneal the LJ system.

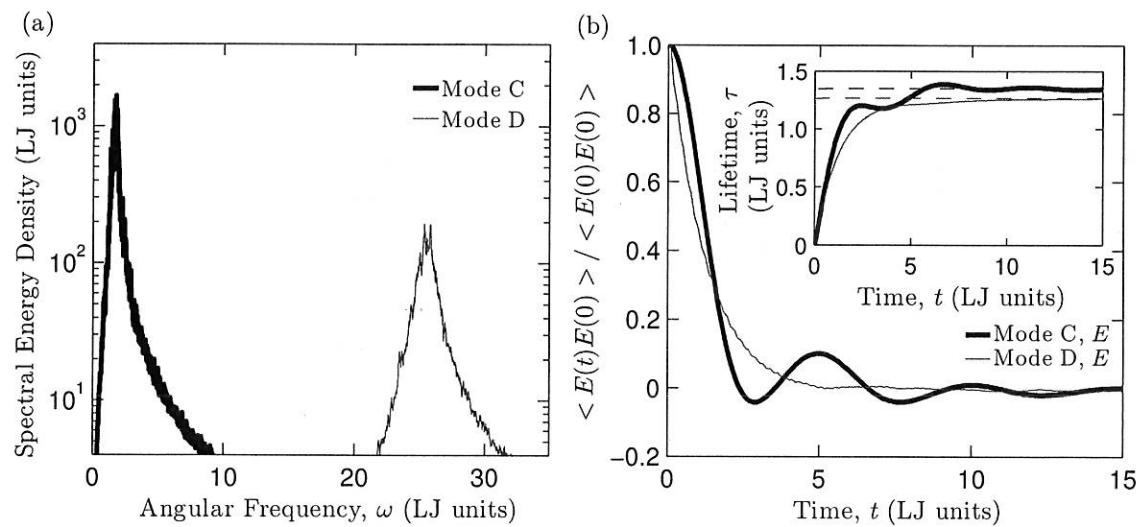


Figure A.3: (a) Time-domain and (b) frequency domain NMD analysis for two modes in an amorphous LJ solid at a temperature of 10 K.

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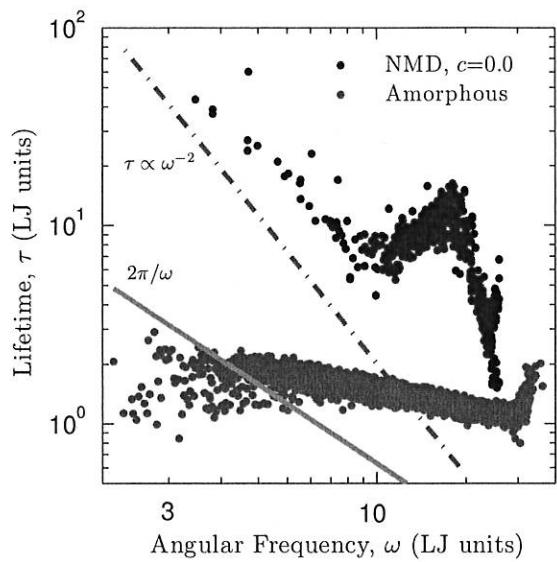


Figure A.4: Lifetimes predicted by normal mode decomposition for an amorphous LJ phase at a temperature of 5 K. The lifetimes for the crystal at a temperature of 10 K are provided for comparison.

## A.5 Finite Simulation-Size Scaling for Thermal Conductivity

The thermal conductivities predicted by the NMD ( $\Phi$ ),  $\Phi'$ , VC-NMD, VC-ALD, and GK methods are system size-dependent [i.e.,  $k = k(N_0)$ ] for all lattices and amorphous materials methods except perfect LJ argon from GK[81] and a-SiO<sub>2</sub> (Section 4.5.1). To predict a bulk thermal conductivity,  $k_{bulk}$ , a linear extrapolation procedure is used, whereby

$$\frac{k(N_0)}{k_{bulk}} = 1 - \frac{c_0}{N_0}, \quad (\text{A.27})$$

- where  $c_0$  is a constant[12, 29, 36, 85]. This procedure is necessary because the first Brillouin zone is only sampled at a finite number of points for a finite simulation size, with no contribution from the volume at its center. To predict a bulk thermal conductivity, it is important to sample points near the Brillouin zone center, where the modes can have large lifetimes and group velocities[12, 123]

The thermal conductivity is predicted for varying system sizes and the bulk thermal conductivity is obtained by fitting Eq. (A.27) to the data. For the NMD ( $\Phi$ ),  $\Phi'$ , VC-NMD, and VC-ALD methods, the validity of Eq. (A.27) requires that the low-frequency modes be dominated by phonon-phonon scattering (i.e.,  $\tau \propto \omega^{-2}$ ) and follow the Debye approximation with respect to the group velocity and DOS[29, 36]. For the LJ argon alloys, this requirement is satisfied for modest system sizes (for  $N_0 = 6$  to 12).

