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Reducing thermal conductivity of binary alloys below the alloy limit via chemical ordering

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Abstract

Substitutional solid solutions that exist in both ordered and disordered states will exhibit markedly different physical properties depending on their exact crystallographic configuration. Many random substitutional solid solutions (alloys) will display a tendency to order given the appropriate kinetic and thermodynamic conditions. Such order–disorder transitions will result in major crystallographic reconfigurations, where the atomic basis, symmetry, and periodicity of the alloy change dramatically. Consequently, the dominant scattering mechanism in ordered alloys will be different than that in disordered alloys. In this study, we present a hypothesis that ordered alloys can exhibit lower thermal conductivities than their disordered counterparts at elevated temperatures. To validate this hypothesis, we investigate the phononic transport properties of disordered and ordered AB Lennard-Jones alloys via non-equilibrium molecular dynamics and harmonic lattice dynamics calculations. It is shown that the thermal conductivity of an ordered alloy is the same as the thermal conductivity of the disordered alloy at ≈0.6T_melt and lower than that of the disordered alloy above 0.8T_melt.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

While thermal conductivity is often a critical property in modern device design, it frequently remains an afterthought. The electrical or optical operating principles of a given device often require specific materials be used; consequently, thermal performance of a device is controlled mainly through packaging techniques [1, 2]. It would be advantageous if thermal transport properties of a material system could be tuned while keeping the constituent materials of that system fixed, thus allowing device-level control over thermal performance. This concept has implications for both current- and next-generation thermal applications, including nanoelectronic cooling [3], solid-state thermal rectifiers [4–7], transistors based on thermal switching [8], thermal memory devices [9], thermoelectric power generators and coolers [10–13], and thermal barrier coatings [14]. In the present work, we demonstrate that device-level control over thermal performance is possible through exploitation of crystallographic reconfigurations associated with order–disorder transitions.

1.1. Crystallography

Substitutional solid solutions (alloys) can exist in both chemically ordered and disordered states. These states, while identical in terms of composition, are distinguished from each other by their unique crystallographic configurations. In the disordered state (random alloy), atoms are randomly distributed among the atomic sites of the crystal, where the probability of finding one type of atom at any atomic site is based on the stoichiometry of the alloy [15]. It is important to
Figure 1. The conventional (top row) and primitive (bottom row) cells of the (a) A1 (FCC), (b) L1₀, and (c) L₁₁ crystallographic configurations. Note that for the L₁₁ system, the conventional cell shown (top (c)) is only one octant of the true conventional cell.

Note that, in this context, disorder does not imply a deviation from crystallinity (i.e., an amorphous solid) since both the ordered and disordered states are fully crystalline. In the ordered state (ordered alloy), atoms are periodically distributed among the atomic sites of the crystal, and each type of atom occupies its own sublattice [16].

The particular crystallographic configuration in which a system will order depends on several factors, e.g., the number and types of constituent atoms comprising the solution, as well as the stoichiometric ratio of the solution itself. Consequently, many configurations have been identified. Face-centered-cubic metallic alloys (A₁, or space group 225) can order into four possible configurations [15, 16], two of which will be covered here (L₁₀, or 123, and L₁₁, or 166). Schematics of these crystallographic configurations are given in figure 1. Although phononic contributions to thermal conductivity in metals are negligible, we would like to note that analogous ordered phases exist in group IV [17–20] and III–V [21–25] semiconductor alloys. That is, the transition from disorder to order in these semiconductor systems is marked by similar reductions in crystallographic symmetry as those in the aforementioned FCC metallic alloys [26, 27]. In turn, semiconductors have been said to exhibit 'L₁₀-type' and 'L₁₁-type' ordering [17–25], where alternating bilayers (instead of monolayers as in the case of the FCC alloys) are distinguishable.

A virtual crystal approach is often taken when describing disordered alloys, especially in the context of x-ray diffraction [28]. Following suit, in disordered AB alloys, an ‘average’ atom with weighted properties of A- and B-type atoms occupies each atomic site of an FCC or A₁ lattice with lattice constant a and an atomic basis of 1. The rhombohedral primitive cell of the A₁ disordered alloy has a volume of $\frac{4}{3}a^3$. Ordered AB alloys in the L₁₀ configuration have an A atom at (0, 0, 0) and a B atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ with regard to the cubic conventional lattice vectors, which are $2a$ in the $x$-, $y$-, and $z$-directions. The volume of the rhombohedral primitive cell is $\frac{4}{3}a^3$, twice that of the A₁ primitive cell. Schematics of the conventional and primitive cells of the A₁, L₁₀, and L₁₁ configurations are shown in figure 1.

1.2. Effects on material properties

The symmetries and periodicities of crystalline materials dictate the Bragg reflection conditions within the crystals. In turn, they influence the propagation and interference of any wavelike quasiparticle and thus the associated material properties. The crystallographic reconfiguration associated with an order–disordered transition causes a distinct and notable change in the Bragg reflection conditions, as evidenced by the changes to diffraction patterns across the transition [16]. Likewise, the order–disorder transition can have a substantial impact on material properties. Many theoretical, experimental, and computational studies have investigated changes in material properties across the order–disorder transition in both metallic and semiconductor systems. These include studies of electrical conductivity [29, 30], electronic band gap [27, 31], optical properties [32, 33], magnetic anisotropy [34], Raman-shift [20, 35, 36], and vibrational properties [37, 38]. Despite these investigations, the role of the order–disorder transitions on phononic thermal conductivity has been left largely unexplored, and while several studies have alluded to the role of order–disorder transitions on thermal conductivity, none have considered it explicitly.

Adachi [39], building upon the phenomenological virtual crystal model established by Abeles [40], investigated the thermal conductivity of several binary, ternary, and quaternary
alloys. It was noted that the deviations between experimental data and the proposed model, which treated only random substitutional solid solutions, were due to atomic ordering. Throughout that study, thermal conductivities were only considered at room temperature, and thus, temperature dependent effects were not studied. McGaughey et al. [41] investigated the phonon band structure and thermal conductivity of a layered Lennard-Jones-type diatomic crystal in the L10 configuration. However, that study drew comparisons only between the L10 system and a homogeneous (monatomic) crystal, not the disordered counterpart. Landry et al. [42] explored thermal conductivity of Lennard-Jones-type superlattices with complex unit cells. Throughout that study, temperature was fixed. Consequently, while they demonstrated that the thermal conductivity of a superlattice with a complex unit cell design could approach the alloy limit at that fixed temperature, the thermal conductivities of the superlattices were never less than the thermal conductivity of the corresponding alloy.

1.3. Present work

In the present study, we have investigated the behavior of phononic thermal transport properties of AB binary alloys in the A1 (disordered), L10, and L11 configurations. These configurations form simple $1 \times 1$ superlattices, as opposed to the complex superlattices discussed by Landry et al. [42]. In section 2, we take a simplified theoretical approach to describe the scenario in which the thermal conductivity of an ordered alloy could be less than that of its disordered counterpart, i.e., reducing the thermal conductivity of a binary alloy below the alloy limit. In section 3, non-equilibrium molecular dynamics (NEMD) simulations are employed to predict the thermal conductivities of ordered and disordered binary Lennard-Jones alloys with a 3:1 A-to-B mass ratio. In addition, harmonic lattice dynamics calculations are implemented to obtain the phonon dispersion and density of states of the ordered configurations. Finally, in section 4, we summarize these results and make our concluding remarks.

2. Theory

The crystallographic reconfiguration across an order–disorder transition is associated with many interrelated phenomena impacting phononic thermal conductivity. These can include a reduction in crystallographic symmetry, formation of a polyatomic basis, a redistribution of vibrational modes, emergence of phononic band gaps, a reduction in phonon group velocity, a reduction in the size of the first Brillouin zone, and a change in the dominant scattering mechanisms. Applying the kinetic theory of gases to a phonon system, thermal conductivity, $\kappa$, can be expressed as

$$\kappa = \frac{1}{3}c_v v l = \frac{1}{3}c_v v^2 \tau,$$

where $c_v$ is the volumetric heat capacity, $v$ is the phonon group velocity, $l$ is the phonon mean free path (MFP), and $\tau$ is the phonon scattering time once all individual phonon scattering processes have been considered [43]. Through consideration of these terms, we will show that the thermal conductivity of an ordered alloy can be less than that of the corresponding disordered alloy due to differences between the dominant phonon scattering mechanisms.

We focus first on the volumetric heat capacity of the lattice. In the classical limit, volumetric heat capacity can be expressed as

$$c_v = 3Nk_B\rho,$$

where $N$ is Avogadro’s number, $k_B$ is the Boltzmann constant, and $\rho$ is the molar density. Since the ordered and disordered crystallographic configurations have both the same average composition and same lattice constant, they have the same molar density and same volumetric heat capacity. Thus, any difference in the thermal conductivities of the ordered and disordered alloys is due to differences in the $v^2\tau$ product.

Before investigating the behavior of the $v^2\tau$ product across the order–disorder transition, we focus on a few phonon fundamentals through a simple example: the one-dimensional atomic chain. Through harmonic lattice dynamics calculations [44, 45], one can derive the phonon dispersion relationship, $\omega(q)$, and phonon group velocity, $v(q) = \partial\omega/\partial q$. We restrict discussion of these quantities (i.e., $\omega(q)$ and $v(q)$) to the confines of the first Brillouin zone (BZ). We make an effort to intentionally avoid use of terms such as ‘extended’ or ‘zone-folded’ while ensuring that the relationship between wavevector in reciprocal space and wavelength in real space ($q = \pi/\lambda$) is upheld throughout the discussion.

Now considering the $v^2\tau$ product, we focus first on the group velocity term. We have implemented harmonic lattice dynamics to calculate $\omega(q)$ and $v(q)$ of two 800 atom long one-dimensional chains, one ordered and one disordered (randomly distributed A and B atoms). Within the chains the interatomic potentials and spacings were defined such that they were the same for all possible interactions ($K_{AA} = K_{BB} = K_{AB}$ and $a_{AA} = a_{BB} = a_{AB}$, respectively) and the mass ratio between A and B atoms was fixed ($m_B/m_A = 3$). Throughout, only nearest neighbor interactions were considered. Periodic boundary conditions were assumed for both the ordered and disordered chains. While the disordered alloy should not exhibit any periodicity, we found that these boundary conditions did not affect our results, i.e., size effects were negligible. The results of these lattice dynamics calculations are presented in figure 2.

In the long wavelength limit, $\lambda \gg a$, phonons do not see the discreteness of the crystal, but rather a continuous medium. At the zone center ($q = 0$, or likewise, $\lambda = \infty$), the group velocity in the ordered and disordered chains is the same, i.e., the sound speed. In a one-dimensional system, sound speed is $v_s = (K/\rho)^{1/2}$, where $\rho$ is the linear mass density. In the ordered alloy and away from the zone center, phonon group velocity is diminished but non-zero (with the exception of the zone center and edge). On the contrary, in the disordered alloy and away from the zone center, phonons are highly localized vibrational modes with negligible group velocity. Despite their higher energy, their group velocity is nearly zero; the contribution of these modes to thermal transport will be negligible (it is important to note that, while localization of this severity is not seen when performing
three-dimensional lattice dynamics calculations of random alloys, a similar reduction in group velocity is realized). Thus, in the event that the ordered alloy (with higher phonon velocities) has a lower thermal conductivity its disordered counterpart, such behavior must be attributed to the scattering time, $\tau$.

Finally, we focus on the phonon scattering mechanisms of ordered and disordered alloys. When considering thermal transport in disordered alloys, it is common practice to take a virtual crystal approach [40]. In this approach, the crystal is viewed as a homogeneous crystal with an average lattice constant and atomic mass. The actual atoms of the alloy are, then, considered impurities within the context of this virtual crystal, acting as phonon scattering centers [44, 46]. Phonon scattering in heavily mixed bulk alloys is dominated by impurity (alloy) scattering [40, 44, 46]. It is important to note that, within the context of this approach, the periodicity of the virtual crystal is such that lattice points are spaced at distances of $a$. Consequently, the first BZ of the disordered alloy spans the range $0 \leq |q| \leq \pi/a$. Determination of selection rules for normal and Umklapp three-phonon scattering events in the disordered one-dimensional alloy require consideration of this description (with regard to the size) of the first BZ.

On the other hand, chemical ordering extinguishes impurity (alloy) scattering due to periodicity. In the ordered state, the primary phonon scattering mechanism will be due to anharmonic three-phonon scattering events and, at high temperatures, Umklapp scattering will dominate. As mentioned above, the prevalence of Umklapp scattering is directly related to the size and shape of the first BZ. In the ordered chain, the lattice constant spans twice the interatomic distance ($2a$). As a result, in the ordered alloy, the first BZ spans the range $0 \leq |q| \leq \frac{\pi}{2a}$, or half the range of the disordered alloy.

Within the context of this discussion, we are able to establish a hypothesis regarding thermal conductivity across the order–disorder transition. With regard to phonon scattering times, the total scattering time can be related to individual scattering times through Matthiessen’s rule [47], given as

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{impurity}}} + \frac{1}{\tau_{\text{Umklapp}}}. \quad (3)$$

In the disordered state, impurity scattering will dominate thermal conductivity across much of the temperature range, although, at elevated temperatures, some signs of Umklapp scattering may be observed. On the other hand, in the ordered state, three-phonon, e.g., Umklapp scattering will dominate thermal conductivity. At elevated temperatures, the rate of Umklapp scattering in the ordered alloy may be greater than the rate of impurity scattering in the disordered alloy due, in part, to the reduction in the size of the first BZ. Due to the different dominant scattering mechanisms and their dependence (or lack thereof) on temperature, the thermal conductivity of the ordered alloy could be less than that of the disordered alloy.

Extending this theory to the three-dimensional configurations of interest, namely, the $A1$, $L1_0$, and $L1_1$ configurations, assuming the difference between the lattice constants of the ordered and disordered states is negligible, the $A1 \rightarrow L1_0$ and $L1_1$ transitions result in a 50% reduction in the volume of the first BZ. This reduction in BZ volume greatly limits the maximum phonon wavevector allowed by the crystal. Due to shape and symmetry, this limitation will be greatest in the [001] direction in the $L1_0$ configuration and the [111] direction in the $L1_1$ configuration. As described above with regard to
one-dimensional systems, this should have a major impact on the phononic thermal conductivity of the ordered alloy due to the different dominant scattering mechanisms of the ordered and disordered states.

3. Present work

To investigate these phenomena and our subsequent hypothesis, we have employed NEMD simulations to study the thermal conductivity of ordered and disordered Lennard-Jones (LJ) binary alloys. NEMD is a technique in which a heat flux is applied across a computational domain and a steady-state, one-dimensional temperature gradient is established. With the thermal flux and temperature gradient known, thermal conductivity can be calculated via Fourier’s law. This technique has been used extensively to investigate thermal transport properties in nanoscopic systems, e.g., thermal conductivity [41, 42, 48–51] and thermal boundary conductance [52–55]. Furthermore, it has been shown that non-equilibrium and equilibrium (Green–Kubo, GK) approaches to predicting thermal conductivity agree so long as the domain is properly sized [48, 56]. Ultimately, the NEMD procedure was chosen over the GK approach due to the inherent difficulty of specifying the converged value of the heat current auto-correlation function when investigating the phononic thermal conductivity [41, 42, 48–51] and thermal boundary conductance [52–55].

While the LJ interatomic potential implemented in this study cannot accurately reproduce the thermophysical properties of many materials beyond inert gases, such simulations are still able to produce meaningful results, especially in the context of phononic (vibrational) properties [41, 42, 50–54].

3.1. Computational details

We have determined the computationally predicted thermal conductivity of AB alloys in the A1 (disordered), L10, and L11 configurations. A- and B-type atoms were distinguished by their atomic masses, which were 40 and 120 amu, respectively. The LJ parameters for the A and B atoms were fixed (ε = 0.0503 eV and σ = 3.37 Å). This approach, where atoms differ only by atomic mass, has been routinely implemented in the literature [41, 53–55, 57, 58]. All results are presented in non-dimensional (reduced LJ) units,

\[
E^* = \frac{E}{\epsilon}, \quad T^* = T\frac{k_B}{\epsilon}, \quad \omega^* = \omega\sqrt{\frac{\sigma^2 m}{\epsilon}}, \quad \kappa^* = \kappa\frac{m^{0.5} \sigma^2}{\epsilon^{0.5} k_B},
\]

where \( m \) is the mass of an A atom (40 amu), and \( E, T, \omega, \) and \( \kappa \), are energy, temperature, angular frequency, and thermal conductivity, respectively. From this point forward the asterisks will be dropped and all results and discussion will make use of non-dimensional units.

The domain sizes were dependent on the crystallographic direction of interest. The A1 and L10 computational domains were \( 31.6 \times 31.6 \times 232 \, \text{Å}^3 \), contained 6336 atoms, and were oriented such that heat flux was applied along the [001] direction. The L11 computational domain was \( 29.8 \times 32.3 \times 237 \, \text{Å}^3 \), contained 6420 atoms, and was oriented such that heat flux was applied along the [111] direction. The four outermost layers of atoms in all domains formed a rigid wall to prevent sublimation from the free surface of the domain during non-equilibrium heating. The eight layers of atoms immediately inside these rigid walls were ‘bath’ atoms, to which energy was added or removed during non-equilibrium heating. Schematics of the computational cells are shown in figure 3. It was subsequently found that any finite size effects were relatively small. Specifically, after increasing the total domain sizes by 50%, thermal conductivities of these larger domains were found to fall near to or within the standard deviations of the thermal conductivities of the smaller domains, depending on the simulation temperature. High temperature simulations were the least affected by finite size constraints.

During the simulation, the equations of motion for the system were integrated using the Nordsieck fifth-order predictor corrector algorithm [59]. Periodic boundary conditions were initially applied in all directions and the system was equilibrated at a predefined temperature via a velocity scaling routine (0.046 \( \leq T \leq 0.47 \), depending on the simulation) and zero pressure. Zero pressure was maintained by the Berendsen barostat algorithm [60]. Once equilibration was complete, the periodic boundary conditions in the \( z \)-direction were switched to free boundary conditions and the system was allowed to thermalize. The addition of energy to/removed from the baths was performed through a constant energy approach, allowing for thermal flux across the computational cell to be controlled explicitly. This routine slightly changes the forces acting on a particular atom depending on the amount of energy to be added or removed.

The total force acting on atom \( i \) is given by

\[
F_{i,\text{total}} = F_i + \xi m_i \nu_i^2,
\]

Figure 3. Schematics of the (a) disordered, (b) L10 ordered, and (c) L11 ordered computational domains. The black atoms at the outer edges represent rigid atoms that ensure no sublimation from the free edges of the domain occurs during the simulation. The darker atoms immediately inside the rigid walls indicate ‘bath’ atoms. The different shading of atoms, red and blue online, in the central region of the domains designates A-type and B-type atoms, respectively.
where \( m_i \) is the mass of the atom, \( v_i^2 \) is the thermal velocity of the atom, and \( \xi \) is a scaling factor. This scaling factor is expressed as
\[
\xi = q \frac{1}{2Kt} = \frac{\Delta E}{2\Delta t K^2},
\]
where \( q \) is the flux across the domain, \( \Delta t \) is the time step used in the molecular dynamics (MD) integration of the equations of motion, \( \Delta E \) is the amount of energy to be added to or removed from the bath per time step, and \( K^2 \) is the total thermal kinetic energy of the bath \cite{61}. To ensure the baths were not being perturbed far from equilibrium they were sized such that the amount of energy added or removed from the bath per time step was less than 1% of the bath kinetic energy. This constant energy approach was preferred over maintaining the baths at a specific temperature because applied flux was known explicitly and not subject to statistical fluctuations, as is the case when baths are maintained at constant temperatures through a thermostat routine.

During non-equilibrium heating, the system was divided into 40 equally sized slices such that a spatial temperature profile could be calculated along the \( z \)-axis. The temperature of each of these slices was determined through the relationship
\[
\frac{1}{2} N_S k_B T_S = \sum_{i=1}^{N_S} \frac{1}{2} m_i (v_i^2)^2,
\]
where \( N_S \) is the number of atoms in a particular slice \( S \), and \( k_B \) is Boltzmann's constant. Each slice was comprised of approximately 100 atoms, but varied slightly due to thermal vibrations causing atoms near slice boundaries to move between neighboring slices. Linear fits of slice temperature, \( T_S \), versus time data were made for discrete time intervals during the simulation and the slopes of these lines were used to determine the onset of the steady-state regime. Once in the steady-state regime, time-averaged spatial temperature profiles were created. To determine the temperature gradient, a linear least squares fit was performed for each temperature profile. The slices (roughly two atomic layers) nearest to the baths were not included in the fits. From the spatial temperature profiles, and with the applied flux known, thermal conductivities of the alloys were calculated via Fourier’s law. The applied fluxes were chosen such that the temperature drop across the domain did not exceed 10% of the average domain temperature. However, this limit was only realized for the lowest temperature simulations; the temperature drop was closer to 4% of the average domain temperature for the majority of the runs.

\[3.2. \text{Density of states calculations}\]

Phonon density of states (DOS) curves of the A1 (disordered), L10, and L11 configurations were calculated in the direction of thermal transport (\( z \)-direction) and are presented in figure 4. The DOS is defined as the Fourier transform of the velocity-correlation function \([53, 62]\) but in practice is calculated using standard estimation procedures for power spectral density. For each atom, the velocity is obtained at each integration time step to give a velocity fluctuation time series of 36,384 points.

The Welch method of power spectral density estimation is then applied by creating eight 50% overlapping segments of 8192 points to give an angular frequency resolution of 0.0029. Each segment is then multiplied by a Hamming window and the fast Fourier transform is computed. The power spectral density, i.e., DOS, is then obtained by ensemble averaging the Fourier transform magnitudes of each segment.

As is shown in figure 4, the phonon DOS curves of both the L10 and L11 ordered alloys differ greatly from that of the A1 disordered alloy, although they do not differ greatly from each other. While the A1 disordered alloy exhibits a fairly flat DOS curve, the DOS curves of the ordered systems exhibit sharp peaks at frequencies 8 and 19 with a deep trough between these peaks. The deep troughs in the curves of the L10 and L11 ordered alloys demonstrate the existence of a phononic band gap between frequencies 12 and 16. This is consistent with the discussion in section 2, where the diatomic basis in an ordered system is responsible for the emergence of phononic band gaps.

\[3.3. \text{Harmonic lattice dynamics}\]

To further investigate the phononic behavior of these systems, we have performed harmonic lattice dynamics \([44, 45]\) (LD) calculations via the General Utility Lattice Program (GULP) software package \([63]\). First, to evaluate the accuracy of the aforementioned DOS calculations, we have once again calculated the phonon DOS of the L10 system via harmonic LD for comparison with the results of the prior MD simulations. In order to directly compare the two methods, we use \( x \)-, \( y \)-, and \( z \)-direction velocity data from the MD simulations to generate a three-dimensional DOS. As is evident in figure 5, the results from the MD simulations and LD calculations are in excellent agreement. We attribute the small discrepancies at elevated frequencies to the anharmonicity of the interatomic potential,
Figure 5. DOS curves of the L10 system via MD simulations and LD calculations, demonstrating that the methods are in excellent agreement. The small discrepancies at elevated frequencies are due to the anharmonicity of the potential, which is considered in the MD simulations, but ignored in the LD calculations.

which is considered in the MD simulations, but ignored in the LD calculations.

In addition to the DOS curves, the cross-plane (in the direction perpendicular to the superlattice) phonon dispersion curves of the L10 and L11 systems were calculated and are presented in figure 6. Calculations were carried out relative to the primitive cells shown in figure 1. Thus, the maximum wavevectors of the L10 and L11 systems in the cross-plane directions are $\pi/a$ and $\sqrt{3}\pi/a$, respectively, where $a$ is the A1 cubic lattice constant. Due to the fact that both the L10 and L11 systems have a two point atomic basis, we can identify six phonon branches (two longitudinal, four transverse) in each system, where the transverse branches are doubly degenerate due to the symmetry in the cross-plane directions of these systems.

3.4. Thermal conductivity

Predicted thermal conductivities of the A1 (disordered), L10, and L11 configurations as a function of reduced temperature from 0.046 to 0.47 are presented in figure 7. Each individual point of the plot represents the mean result of five independent simulations. Error bars represent the standard deviation of thermal conductivity predictions, i.e., repeatability. The thermal conductivity of the A1 alloy is only weakly a function of temperature, while the thermal conductivities of the ordered alloys exhibit an inverse-temperature-type dependence, indicative of Umklapp dominated conductivity. The thermal conductivities of the two ordered alloys are equal to the thermal conductivity of the disordered alloy at $T \approx 0.3$, or 60% of the melting temperature (the melting temperature of LJ solids $\approx 0.5$ [53]). In addition, and perhaps of greater interest, the thermal conductivities of the two ordered alloys are lower than that of the disordered alloy at $T > 0.4$, or 80% of the melting temperature. These results suggest that increased order can result in a decrease in the thermal conductivity of a binary alloy below the alloy limit at elevated temperatures.

It is also interesting to note that the cross-plane thermal conductivities of the L10 and L11 systems are nearly identical, despite the different atomic configurations of these two systems. While both systems are $1 \times 1$ superlattices, the direction of superlattice formation is different. In the case of the L10 system, the superlattice forms in the [001] direction, a non-close-packed direction. In the case of the L11 system, the superlattice forms in the [111] direction, a close-packed direction. While this distinction manifests itself in the cross-plane phonon dispersion curves, it does not manifest itself in either the phonon DOS curves or the thermal conductivity predictions.

To further identify the aforementioned convergence and crossover of thermal conductivities, we have performed inverse power fits ($\kappa = \beta T^{-1} + \gamma$, where $\beta$ and $\gamma$ are variable)
of the ordered reduced thermal conductivities and a linear fit of the disordered reduced thermal conductivities. These fits, along with confidence intervals, are presented in figure 8. Each fit was constructed using a sample size of 40, with each sample corresponding to an independent NEMD simulation. The crossover of the L10 and L11 inverse power fits with the A1 disordered linear fit occurs at \( T = 0.39 \). In order to quantify the uncertainty in the curves and assess their goodness-of-fit, simultaneous confidence intervals were calculated at a 95% level over the range of fitted values (0.21 \( \leq T \leq 0.40 \)). These confidence values correspond to the hypothesis that the upper and lower confidence bounds contain the true best-fit regression curve 95% of the time. These confidence intervals are represented graphically in figure 8 as dashed lines that surround each fit.

4. Conclusion

We have presented thermal conductivity predictions of ordered and disordered binary Lennard-Jones alloys calculated via non-equilibrium molecular dynamics simulations. The results of these simulations indicate that the thermal conductivity of a random binary alloy can be subsequently lowered at high temperatures. We attribute this behavior to the different phonon scattering mechanisms that dominate thermal conductivity in the ordered and disordered systems, behavior consistent with elementary phonon theory. This concept is technologically rich, especially in the field of thermoelectric power generation and cooling, where reduced thermal conductivities are sought. However, a few caveats must be mentioned. First, it remains essential to determine the temperature at which atomic ordering can be preserved. Second, and with respect to thermoelectric devices, the true merit of ordered alloys may rest not in the observed reduction in thermal conductivity, but the plausible increase in electrical conductivity due to ordering, thus increasing the overall figure of merit. Lastly, the second-rank tensorial properties within these domains (thermal and electrical conductivity) will be anisotropic. Consequently, orientation could play a critical role in any application.

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