ABSTRACT
The phononic band structure and thermal conductivity of a family of a two-atom unit cell Lennard-Jones crystals are predicted using molecular dynamics simulations. The structure consists of alternating layers of atoms with different masses, leading to anisotropic thermal properties. An increase in the mass ratio results in an increase in the width of the band gap and a decrease in the value of its central frequency. The thermal conductivity decreases with an increase in the mass ratio, and in all cases is lower than that for a monatomic unit cell. The thermal conductivity increases with an increase in the ratio of the central gap frequency to its width. The rate of this increase decreases and becomes less temperature-dependent at lower mass ratios. The results could be utilized towards the development of guidelines for the design of materials with extreme thermal transport properties.

NOMENCLATURE
\( a \) lattice constant
\( A \) constant
\( B \) constant
\( E \) energy
\( F \) force vector
\( k \) thermal conductivity
\( k_B \) Boltzmann constant
\( K \) spring constant
\( m \) mass
\( m^* \) mass ratio
\( N \) number of atoms
\( r, r \) particle position, particle separation, particle separation vector
\( S, S \) heat current, heat current vector
\( t \) time
\( T \) temperature
\( v \) particle velocity vector
\( V \) volume

Greek
\( \Delta \) band gap
\( \epsilon_{\text{LJ}} \) Lennard-Jones energy scale
\( \kappa \) wave number
\( \sigma_{\text{LJ}} \) Lennard-Jones length scale
\( \tau \) time constant
\( \phi \) potential energy
\( \omega \) angular frequency

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Numerous experimental studies have found similar results [i.e., that guest (rattler) atoms can reduce the conductivity] (e.g., [6, 7]). Apart from these efforts, there have been very few investigations that have attempted to rigorously establish the connection between dispersion characteristics, which include the size and location of band gaps, as well as velocity quantities, and thermal transport properties.

The present work explores the three-way relationship in a crystal between: (i) the unit cell structure and properties, (ii) the associated dispersion characteristics, and (iii) the bulk thermal transport behavior. As a starting point, attention is narrowed to a two-atom unit cell. By modeling simple systems, phenomena can be observed that might not be discernable in more complex structures. A Lennard-Jones (LJ) system containing two different masses is considered. Insights from the present study could lead to the development of a systematic technique for the atomic-level design of materials with desired thermal transport properties. This capability could facilitate the introduction of novel, yet realizable, materials with extremely high, or low, thermal conductivities. Examples of applications include electronic devices enjoying enhanced cooling characteristics and efficient thermal insulators for chemical processing. In the context of the continuum description of periodic materials, the idea of tailoring the frequency band structure has previously been applied in the areas of electromagnetics [8] and elastodynamics [9-11].

We begin by introducing the basic formulations for the MD simulations and thermal conductivity prediction method [the Green-Kubo (GK) approach]. The zero-temperature LJ phonon dispersion curves are then computed for different mass ratios. This is followed by the prediction of thermal conductivity for the different mass ratios over a wide range of temperatures. Discussion is presented with regards to the magnitude of the thermal conductivity, its directional dependence, and relation to the unit cell. The relationship between the thermal conductivity and the associated band structure is then explored. We conclude with a discussion of future research directions.

Molecular Dynamics Simulations

In an MD simulation, the classical position and momentum space trajectories of a system of particles are determined using interatomic forces (which are calculated from an appropriate interatomic potential) and the Newton laws of motion. Here, systems described by the LJ potential,

\[
\Phi_{ij}(r_{ij}) = 4\epsilon_{LJ} \left[ \left( \frac{\sigma_{LJ}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{LJ}}{r_{ij}} \right)^{6} \right],
\]

are considered. In Eq. (1), \( \Phi_{ij} \) is the potential energy associated with a pair of particles \( (i \text{ and } j) \) separated by a distance...
The net flow of heat in the MD system, given by the heat current vector $\mathbf{S}$, fluctuates about zero at equilibrium. In the GK method, the thermal conductivity is related to how long it takes for these fluctuations to dissipate. For the two-atom unit cell under consideration, the thermal conductivity, $k$, will be anisotropic (different in directions perpendicular and parallel to the planes) and for a direction $i$ will given by [14]

$$k_i = \frac{1}{k_B VT^2} \int_0^\infty \langle S_i(t)S_i(0) \rangle dt,$$

(2)

where $k_B$ is the Boltzmann constant, $t$ is time, $T$ is temperature, and $\langle S_i(t)S_i(0) \rangle$ is the heat current autocorrelation function (HCACF) for the direction $i$. Parallel to the planes, the HCACF can be averaged over the [010] and [001] directions. The heat current vector for a pair potential is given by [14]

$$\mathbf{S} = \frac{d}{dt} \sum_i E_i \mathbf{r}_i = \sum_i E_i \mathbf{v}_i + \frac{1}{2} \sum_{ij} (\mathbf{F}_{ij} \cdot \mathbf{v}_i) \mathbf{r}_{ij},$$

(3)

where $E_i$, $\mathbf{r}_i$, and $\mathbf{v}_i$ are the energy, position vector, and velocity vector of particle $i$, and $\mathbf{r}_{ij}$ and $\mathbf{F}_{ij}$ are the inter-particle separation vector and force vector between particles $i$ and $j$.

**ZERO-TEMPERATURE PHONON DISPERSION**

The zero-temperature phonon dispersion curves corresponding to the longitudinal and transverse polarizations in the [100] direction for $m^*$ values of 1, 1.5, and 10 are shown in Figs. 2, 3(a), and 3(b). A dimensionless wave number $\kappa^*$ has been defined such that $\kappa^* = \kappa/(2\pi/a)$, where $a$ is the lattice constant (see Fig. 1). The dimensionless frequency $\omega^*$ is in LJ units. In the frequency labels in the plots, the subscripts $L$, $T$, $ac$, and $op$ refer to longitudinal, transverse, acoustic, and optical. The minimum frequency of the optical branches is independent of the mass ratio. This is a result of the optical modes at the edge of the first Brillouin zone only involving the motion of the $m_2$ atoms, whose mass is fixed, and is consistent with the dispersion characteristics of a two-atom one-dimensional mass-spring system [15].

While the thermal transport is anisotropic, the dispersion characteristics in the [100], [010], and [001] directions are the same. For $m^*$ values greater than unity, the longitudinal and transverse curves split into acoustic and optical branches. Beyond a mass ratio of 1.97, a band gap exists between the acoustic and optical branches [shown in Fig. 3(b)]. The width of the band gap is denoted by $\Delta_{full}$, and its center as $\omega^*_{gap,full}$. The maximum frequencies of the longitudinal acoustic and optical branches are plotted in Fig. 4(a) for $m^*$ values between unity and 100. The size of the band gap and the location of its center are plotted in
THERMAL CONDUCTIVITY PREDICTION

Thermal Conductivity Decomposition in GK Method

The most significant challenge in the implementation of the GK method is the specification of the integral in Eq. (2). This may be a result of not obtaining a proper sampling of the system’s phase space, even when averaging over a number of long, independent simulations. Thus, it is not always possible to directly specify the thermal conductivity. Other approaches have been suggested, including the first dip approach [16] and the fitting of the HCACF to a set of algebraic functions [13, 17, 18].

Here, both the direct specification and fitting techniques are used. It has been shown [13, 17, 18] that the thermal conductivities of the monatomic LJ fcc crystal and a family of complex silica structures can be decomposed into contributions from short and long time scale interactions by fitting the HCACF to a function of the form

\[
\langle S(t) \cdot S(0) \rangle \equiv A_{ac,sh} \exp(-t/\tau_{ac,sh}) + A_{ac,lg} \exp(-t/\tau_{ac,lg}) + \sum_i B_{op,i} \exp(-t/\tau_{op,i}) \cos(\omega_{op,i} t) \quad (4)
\]

This decomposition can also be performed for the components of the HCACF in a specific direction. Here, the subscripts \(sh\) and \(lg\) refer to short-range and long-range. The \(A\) and \(B\) parameters are constants, and \(\tau\) denotes a time constant. The optical phonon term is used when appropriate (i.e., for crystals with more than one atom in the unit cell). The summation in the optical phonon term corresponds to the peaks in the Fourier transform of the HCACF. Using Eqs. (2) and (4),

\[
k = \frac{1}{k_B VT^2} \left( A_{ac,sh} \tau_{ac,sh} + A_{ac,lg} \tau_{ac,lg} + \sum_i \frac{B_{op,i} \tau_{op,i}}{1 + \tau_{op,i}/\omega_{op,i}^2} \right) \quad (5)
\]

\[
\equiv k_{ac,sh} + k_{ac,lg} + k_{op}
\]

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Further details on the decomposition can be found elsewhere [13, 18].

**Heat Current Autocorrelation Function**

The HCACF (normalized by its zero time value), its integral (the thermal conductivity), and the real part of its Fourier transform are shown for three cases in Figs. 5, 6, and 7.

The data in Fig. 5 correspond to the monatomic unit cell at a temperature of 50 K. The HCACF decays monotonically, and is fit well by the sum of two decaying exponentials. The fits to the HCACF and its integral (the thermal conductivity) are shown in the plot and match the raw data well. Such behavior is found at all temperatures considered. The real part of the Fourier transform of the HCACF has its maximum value at zero frequency, and decays to zero beyond that, consistent with the spectrum of an exponential decay.

The data in Fig. 6 correspond to the \( m^* = 1.5 \) unit cell at a temperature of 20 K in the direction parallel to the planes. Oscillations in the HCACF are now present, which are an effect of the optical phonon modes. The Fourier transform has a similar low frequency behavior to the monatomic unit cell, but there is a sharp peak in the upper region of the spectrum. The HCACF can be fit with an expression of the form of Eq. (4), with one term taken in the summation. The fits to the HCACF and the thermal conductivity are shown in Fig. 6(a). Such fits were found to be possible for all cases with \( m^* \) values of 1.5 and 2, and the direction parallel to the planes with \( m^* \) values of 5 and 10. The agreement between the fit thermal conductivity and that specified directly from the integral is almost always within 10%.

The data in Fig. 7 correspond to the \( m^* = 10 \) unit cell at a temperature of 40 K in the direction perpendicular to the planes. There are large oscillations in the HCACF. The Fourier transform is now dominated by broad band behavior at high frequency, and the low frequency behavior is more difficult to resolve. Fitting the oscillations in the HCACF with a set of exponentially decaying sinusoids is not possible due to the wide range of frequencies excited, and the broadness of the peaks. The thermal conductivity in this situation, which exists for the direction perpendicular to the planes for \( m^* \) values of 5 and 10, must be specified directly from the integral. The integral shown in Fig. 7(a) converges at a longer time than shown in the plot. This indicates that while the oscillations in the HCACF dominate its magnitude, that the contribution of the \( k_{ac,lg} \) term is significant, even if it cannot be resolved in the raw HCACF. This failure of the fitting procedure was not found in the investigation of the silica structures [18]. In that case, all the peaks remained well-defined over the temperature range considered, and did not interfere with the low frequency behavior. This may be due to the large unit cells studied there, which have a broader range of optical phonon frequencies that will not interfere with the low frequency behavior.

**Thermal Conductivity Trends**

When applicable, the thermal conductivity decomposition according to Eq. (5) leads to similar results as those found previously [13, 18]. These will be discussed in future work, and we now move to a discussion of the bulk results.

The thermal conductivities predicted for the \( m^* = 1.5 \) system are plotted in Fig. 8(a) along with the data for the monatomic unit cell. The thermal conductivities for all cases considered in the direction perpendicular to the planes are plotted in Fig. 8(b). The data are fit with power law functions, and these curves are...
shown to guide the eye. Due to the classical nature of the simulations, all the curves will go to infinity at zero temperature.

The thermal conductivities parallel and perpendicular to the planes are lower than the monatomic value. Generally speaking, as found by Dong et al. [5], a more complicated unit cell leads to increased phonon scattering, which will decrease the thermal conductivity. The deviation from the monatomic value increases as the mass ratio increases. In the limit of an infinite mass ratio, the thermal conductivity will go to zero. This limit, and the overall behavior, can be understood from the trends in the dispersion curves. As the mass ratio increases, the branches get flatter. The phonon velocities (related to the slope of the dispersion curves) will get correspondingly smaller until they reach a value of zero when the branches are completely flat, leading to zero thermal conductivity. In general, the effect of the mass ratio suggests that while designing for a desired thermal conductivity is a suitable goal, values above that for the simple base system are unlikely to be found. When a somewhat ideal, uniform structure is altered, additional scattering mechanisms will always be introduced.

At $m^* = 1.5$, the thermal conductivity perpendicular to the
planes is higher than that parallel to the planes. This is an indication of the anisotropic nature of the phonon scattering, and warrants further investigation. As the mass ratio is increased, the thermal conductivities in the two directions approach the same value. The effect of the smaller mass ($m_2$) is becoming less and less, and the crystal structure starts to resemble a monatomic cubic crystal, which will be isotropic from a thermal transport perspective. As the mass ratio goes to unity, the atoms become the same, and the system begins to resemble the fcc crystal. In this case, the thermal conductivity will also be isotropic.

Figure 7. (a) HCACF AND THERMAL CONDUCTIVITY FOR THE $m^* = 10$ UNIT CELL AT A TEMPERATURE OF 40 K IN THE DIRECTION PERPENDICULAR TO THE PLANES. THE FITTING PROCEDURE WAS NOT POSSIBLE FOR THIS CASE. (b) REAL PART OF THE FOURIER TRANSFORM OF THE HCACF. THE QUASI-HARMONIC DISPERSION CURVES IN THE [100] DIRECTION ARE ALSO SHOWN.

We note that Che et al. [17] have performed a set of similar simulations with carbon atoms in the diamond structure. They vary the masses of the atoms in the unit cell such that the density of the system remains the same as for the monatomic state. The results are qualitatively similar to those found here.
THE LOCATION OF THE PEAKS IN THE REAL PART OF THE HCACF FOURIER TRANSFORM PLOTTED WITH THE RANGE OF THE OPTICAL PHONON BRANCHES FOR THE \( m^* = 1.5 \) SIMULATION CELL.

CORRELATION BETWEEN BAND STRUCTURE AND THERMAL CONDUCTIVITY

Dispersion and Heat Current Autocorrelation Function

While peaks in the spectrum of the HCACF have been observed [17-19], no comprehensive explanation has been given for their origin. In [18] it was hypothesized that they corresponded to optical phonons, due to their frequencies lying in that region of the spectrum. In Fig. 9, the location of the peak as a function of temperature is plotted along with the maximum and minimum frequencies of the optical phonon branches for the mass ratio of 1.5. The extent of the transverse optical phonon branch and the HCACF Fourier transform are shown together in Fig. 6(b) for the \( m^* = 1.5 \) system at a temperature of 20 K. The finite temperature dispersion data correspond to a quasi-harmonic calculation [20]. This will introduce some error, which will grow with temperature. The calculation of the anharmonic dispersion curves is a significant computational task [3], and would not add to the qualitative nature of this discussion.

The frequencies corresponding to the direction perpendicular to the planes are well bounded by the longitudinal data. This implies that it is the motion of atoms perpendicular to the planes that are generating the peaks. The frequencies corresponding to the direction parallel to the planes are well bounded by the transverse data. This also implies that it is the motion of the atoms perpendicular to the planes that is generating the peaks. Further investigation of this interesting behavior is being pursued.

At the higher temperatures, the optical branches become narrow [see Fig. 3(b)]. As well, the peaks in the HCACF spectrum become broad [see Fig. 7(b)] and it is difficult to associate a single frequency with them. Thus, as shown in Fig. 7(b), while the excited region in the spectrum covers the optical bands, the center of the peak does not necessarily fall within one of them.

These results indicate that it is the optical phonon modes that generate the peaks. While they may not make a significant contribution to the thermal conductivity, they do introduce scattering that reduces its magnitude.

Dispersion and Thermal Conductivity

The thermal conductivity perpendicular to the planes is plotted versus the full band gap width in Fig. 10(a), and verses the frequency at the center of the full band gap in Fig. 10(b) for mass ratios of 2, 5, and 10. The \( m^* = 1.5 \) system does not have a full band gap [see Fig. 3(a)]. For all temperatures considered, the thermal conductivity decreases with an increase in the bandgap size - an expected result as the range of allowed frequencies is decreasing. On the other hand, the thermal conductivity increases with an increase in the gap central frequency. Noting that the minimum optical transverse frequency is independent of the mass ratio, the trends in Figs. 10(a) and 10(b) are seen to be consistent with each other. The collective effect of the band-gap size and its location is demonstrated in Fig. 11, where the thermal conductivity is plotted as a function of the ratio of the central gap frequency to its width, \( \omega_{\text{op,L}}/\Delta \omega_{\text{full}} \), a commonly used metric in the photonic crystal literature. A noteworthy feature in this plot is the trend towards saturation of the temperature curves as this frequency ratio increases. Further simulations are planned for mass ratios less than unity to fully capture this behavior, and what it might indicate in the context of thermal conductivity limits.

SUMMARY

Lennard-Jones crystal structures composed of alternating layers of atoms with different masses have been studied. The width of the phonon band gap is found to increase as the mass ratio increases, while the frequency at the center of the gap decreases. The trends are consistent with than those predicted for a one-dimensional mass-spring model.

Subsequently, MD simulations and the GK method have been employed to predict the thermal conductivity of these structures. As shown in Figs. 8(a) and 8(b), the thermal conductivity decreases with an increase in the mass ratio, and in all cases the values are lower than the predictions for the associated monatomic unit cell.

Finally, the possible correlation between the phonon band structure and the thermal conductivity has been investigated. Peaks in the spectrum of the HCACF are seen to occur within the range of the optical phonon branches (see Fig. 9). As shown in Fig. 11, the thermal conductivity is observed to rise with an increase in the ratio of the central gap frequency to its width.
The rate of this increase decreases and becomes less temperature-dependent at low mass ratios.

Future work will include: (i) a further investigation of directional effects in connection to both real and frequency properties, (ii) incorporation of anharmonic dispersive effects, and (iii) consideration of complex unit cell structures. The long term goal is the exploitation of these studies towards the development of guidelines for the design of dielectric materials with extreme thermal transport properties.

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