MOLECULAR DYNAMICS SIMULATION OF THERMAL CONDUCTIVITY OF NANOCRYSSTALLINE COMPOSITE FILMS

N.A. Roberts, D.G. Walker and D.Y. Li
Department of Mechanical Engineering
Vanderbilt University
Nashville, TN USA, 37235

ABSTRACT
The effectiveness of a thermoelectric device is measured by the figure of merit ZT, which is inversely proportional to the thermal conductivity. Superlattice materials often have a reduced thermal conductivity because of the introduction of interface scattering and, therefore, improved performance. The present work is focused on the effective thermal conductivity of nanocomposite films. This configuration could also improve ZT because of phonon-interface scattering introduced by the nanocrystals. The effects of crystal size and mass fraction is studied numerically using a molecular dynamics simulation. Results indicate that a reduction in the effective thermal conductivity can be achieved with the addition of a nanocrystal.

NOMENCLATURE

\( a \) lattice constant (m)
\( k \) thermal conductivity (W/mK)
\( L \) device length (m)
\( N \) number of atoms
\( n \) number fraction
\( r \) interatomic distance (m)
\( rcut \) cutoff radius (m)
\( S \) Seebeck coefficient (\( \mu \)V/K)
\( T \) temperature (K)
\( U \) interatomic potential (J)
\( ZT \) thermoelectric figure of merit
\( \varepsilon \) energy parameter (J)
\( \sigma \) lattice parameter (m)
\( \xi \) crystal radius (m)

INTRODUCTION
Nanostructured materials hold great promise for high performance thermoelectric energy conversion devices. Nanocrystalline composites (NCC), which are bulk materials with embedded nanoparticles, may provide a favorable combination of effects that result in significant improvements in thermoelectric performance [1]. In particular, these materials show a decrease in thermal conductivity, which is inversely proportional the thermoelectric figure of merit (ZT). Two recent experiments [2, 3] have shown that single crystalline composite materials with embedded nanoparticles or quantum dots exhibit an increased thermoelectric figure of merit (\( ZT \approx 2 \)). This performance is in sharp contrast to that of previous efforts that use alloys to improve thermoelectric energy conversion yielding values for \( ZT \) no larger than 1 at room temperature [4]. This dramatic improvement is, in large part, a result of the reduction in the thermal conductivity.

Measurements of thermal conductivity in superlattices have also shown a significant reduction, and the mechanisms for this reduction include interface scattering [5, 6], phonon phase interference introduced by the periodicity of the lattice [7], or phonon band creation [8]. Molecular dynamics studies by Chen et al. [9] suggest that the reduction is largely diffuse scattering at the interface for lattice mismatched materials. For lattice matched materials, phonon interference and phonon band formation dominate and a minimum occurs for a period length comparable to the dominant phonon wavelength.
For nanocrystalline composites, the scattering mechanism is not likely a wave interference phenomenon. Instead, the scattering is particle-like because the periodicity in [3] is much larger than the phonon wavelength. The added particles, then, must be particularly efficient scatterers. Their theory is that the scattering rate is proportional to the scattering cross section, which is related to the particle size. The size dependence of the scattering in [3] supports their hypothesis. However, detailed analysis has yet to confirm this premise.

The present effort systematically studies the effect of the size of nanoparticles with molecular dynamics for phonon transport. The present work seeks to examine the thermal transport aspect of the thermoelectric performance issue in nanocomposite materials. The analysis involves a molecular dynamics study of a periodic array of crystals of varying sizes and atomic number fraction. In particular, we want to examine and explain the reduction in the thermal conductivity of NCC and understand how the structure exhibits a thermal conductivity lower than the allowed limit.

**ANALYSIS**

In the present work, the effective thermal conductivity of a composite material is investigated using molecular dynamics [10]. The composite structure is composed of a matrix material (Ar) with embedded nanocrystals of a different material (Kr). In one set of simulations, the nanocrystal is located at the center of the wire and the radius \( \xi \) is systematically varied. In another set of simulations, half of the atoms are of one type and the other half of the other type. For this fixed number ratio, the size of the continuous regions of similar types is varied. Figure 1 shows the various structures investigated in this study.

An FCC crystalline structure is assumed with a Lennard-Jones interatomic potential given as

\[
U = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right].
\]

The devices contain two materials whose property values are given in Table 1. The film is treated as a periodic lattice in the plane perpendicular to transport. In the transport direction, the device is finite.

For the simulations, a time step of 1 fs for 400,000 time steps was used where the data begins recording after 20,000 time steps to reach a quasi-steady state. The time step and length of the simulation (0.4 ns) were obtained from the thermal relaxation time of argon. The size of the device used for these simulations was \( 8 \times 8 \times 8 \) unit cells with an additional 10 unit cells (5 on each side) in the direction of transport for the wall and bath. This configuration was used to minimize the impact of the boundaries on the thermal conductivity which has was verified by Lukes [11].

### Table 1. Parameters used for the different materials in the simulations [10]. For potentials between different atoms, the energy parameter \( \varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} \) and the length parameter \( \sigma_{12} = (\sigma_1 + \sigma_2)/2 \).

<table>
<thead>
<tr>
<th>Material</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>( \varepsilon ) (J)</td>
<td>( 2.25 \times 10^{-21} )</td>
</tr>
<tr>
<td></td>
<td>( \sigma ) (m)</td>
<td>( 3.65 \times 10^{-10} )</td>
</tr>
<tr>
<td></td>
<td>( a ) (m)</td>
<td>( 5.69 \times 10^{-10} )</td>
</tr>
<tr>
<td></td>
<td>( m ) (kg)</td>
<td>( 1.39 \times 10^{-25} )</td>
</tr>
<tr>
<td></td>
<td>( r_{cut} ) (m)</td>
<td>( 9.49 \times 10^{-10} )</td>
</tr>
<tr>
<td>Ar</td>
<td>( \varepsilon ) (J)</td>
<td>( 1.67 \times 10^{-21} )</td>
</tr>
<tr>
<td></td>
<td>( \sigma ) (m)</td>
<td>( 3.4 \times 10^{-10} )</td>
</tr>
<tr>
<td></td>
<td>( a ) (m)</td>
<td>( 5.3 \times 10^{-10} )</td>
</tr>
<tr>
<td></td>
<td>( m ) (kg)</td>
<td>( 6.63 \times 10^{-25} )</td>
</tr>
<tr>
<td></td>
<td>( r_{cut} ) (m)</td>
<td>( 8.84 \times 10^{-10} )</td>
</tr>
</tbody>
</table>

The entire device is composed of 4,608 atoms, 2,560 are wall and bath atoms. The bath temperatures are held constant at 40 K and 60 K for the cold and hot sides respectively, with an initial temperature of 50 K.

The effective thermal conductivity is calculated from Fourier’s law for steady conduction,

\[
q = -k A \frac{\Delta T}{L},
\]

where \( L \) is the length of the device between the two constant bath layers. Fourier’s is assumed to be valid due to the relatively constant behaviour of the heat flux through each plane within the domain. The heat transfer \( q \) is found using the non-equilibrium molecular dynamics approach outlined by Ikeshoji [12], and the temperature is found by totaling the kinetic energy in the bath. Using kinetic arguments, the temperature is found from

\[
\frac{3}{2} N k_B T = \sum_i \frac{1}{2} m_i v_i^2,
\]

\( N \) is the number of atoms in each bath. In contrast to the technique provided by Ikeshoji [12], our bath is held at a constant temperature by adjusting the energy added at each time step. As such, the temperature difference in equation 2 is fixed and the heat flux can be obtained from the running average of the amount of energy added to maintain that temperature difference. The flux is averaged over long times [11] to establish a stable value for the heat flux.
The crystal consists of krypton and the surrounding lattice is ar-

tered to the mean free path of phonons \([13]\). Although the pres-

t to argon, therefore as the number of krypton atoms increases,

These two effects can be summed if the thermal re-

cative to the increase in interface area. This feature indicates that
the lattice mismatch between the krypton and argon, an addi-
tual thermal resistance is introduced in the form of inter-
face-phonon scattering \([10]\). These two effects can be summed if
the thermal resistance is considered instead of the thermal con-
ductivity. The total resistance is then written as

\[
R_{\text{tot}} = R_m + R_i,
\]

where \( R_m \) is the contribution from the bulk material proper-
tures and \( R_i \) is the contribution from the interface.

In general, the resistance due to multiple materials \( R_m \)
materials depends on the geometry of the constituents. In the limi-
ting cases of purely parallel and series heat transfer, the effective
resistance can be significantly different. In the case of similar
conductivities, however, the parallel and series models reduce to
give similar results. Because the conductivity of krypton is only
10\% larger than that of argon, a series model is used for its sim-
plicity. Consequently, the material resistance from equation 4
is found by adding the contributions from each component as

\[
R_m = \frac{L}{A} \left( \frac{1-n}{k_1} + \frac{n}{k_2} \right),
\]

where \( n \) is the fraction of atoms in the material with conduc-
tivity \( k_2 \). For crystal diameters less than the device length, the number
fraction is approximately the volume of the crystal divided by
the volume of the device, so \( n \) increases as the cube of the radius \( \xi \).
The length \( L \) and area \( A \) are the length and cross sectional area
of the device, respectively.

The interface resistance is presumably a function of the in-
terface area and is expressed as a jump condition

\[
R_i = A_i \frac{\Delta T}{q} = \gamma A_i,
\]

where \( g \) is the heat flux through the interface, which is the same
as in equation 2. In the present case, the temperature drop \( \Delta T \)
across the interface is unknown. Therefore, we introduce a fitting
parameter \( \gamma \) to account for the non-uniformity. The surface area
increases as \( A_i = 4\pi \xi^2 \) until \( \xi = L/2 \), which is the radius of an
scribed sphere (crystal) in a cube (device). At this point, the area
decreases through \( \xi = L/\sqrt{2} \) (the midradius) until \( \xi = \sqrt{3}L/2 \)
(the radius of the circumscribed sphere) where the entire device
is composed of krypton, which is the crystal material. Realize
this model assumes that interfaces parallel to the transport di-
rection contribute to the thermal resistance equally as much as
the interfaces perpendicular to the flow. Experiments at reduced
scales have shown that boundary resistance plays a significant
part in reducing the overall thermal conductivity of a device. This
effect can dominate in devices with characteristic lengths compa-

table to the mean free path of phonons \([13]\). Although the present
case does not have true boundaries parallel to the transport di-
rection, the crystal creates a scattering interface that is conduc-
tive to this type of thermal resistance.

An estimate of the effective conductivity is found from equa-
tion 4 as

\[
k_{\text{eff}} = \frac{L}{(R_m + \gamma A_i)A}.
\]

The results of the molecular dynamics conductivity study as
a function of crystal size are shown in Figure 2 with the first order
model from equation 7. The fitting parameter \( \gamma = 0.01 \text{K/m}^2\text{W} \)
and the normalized conductivity of krypton \( k_{K_r} = 1.13 \) were set
to achieve the comparison. The analytic model, however, does
not consider phonon interference effects and multi-dimensional
transport, so perfect agreement is not expected. Nevertheless,
we observe a decrease in conductivity that appears to corres-
d to the increase in interface area. This feature indicates that
the crystal/matrix interface plays a critical role in the effective the-
mal conductivity of the device.

The fitting parameter \( \gamma = 0.01 \) was chosen to provide a good
match in the region where the crystal is smaller than the device.
For larger radii, the fit is not as good. This could be due to the

Figure 1. Two-dimensional representation of different configura-
tions considered for effective thermal conductivity calculations. In configuration I, the radius \( \xi \) is varied. In configuration II, the period of the alternating blocks is varied, and mass fraction is held constant.
fact that the bath interacts with both krypton and argon where the crystal size exceeds the device size. Consequently the bath may transfer more of its energy into the krypton and through the crystal. In this case, the bath is no longer a uniform temperature source/sink and the concept of continuum resistance as a function of area (equation 4 is no longer valid).

So far our premise is that the interface between materials results in additional scattering that decreases the effective thermal conductivity. To test this, we performed a series of simulations where the atoms were distributed randomly in the device (see Figure 3), but the fraction of krypton atoms was systematically varied. The results are shown in Figure 4. In this case, an interface area is meaningless, but we see the same characteristic decrease in the conductivity. In fact, the conductivity decreases much more. One could argue that the area of interfaces is actually quite large compared to the crystal case, and therefore, the conductivity is significantly lower. This behavior suggests that this simple system can not beat the alloy limit [3]. To investigate this premise, configuration II was used to vary the size of the crystals in the device. For this simulation the fraction of krypton atoms was held constant at 50% and the number of crystals was varied. Because our simulation domain was so small, we were limited to 3 cases. We fixed the period length of the cubic crystal to 1, 2 and 4. Figure 5 shows the results as a function of the interface area. The area available for phonon scattering is estimated as the area of a single crystal face times the number of crystals times 6 sides per crystal. By varying the crystal and placing more crystals in the domain, we can increase the area for scattering greatly. As a result we see a marked decrease in conductivity. However, these data for the highest areas are essentially the same as the randomly distributed 50% case and the conductivity is the same. Again this result suggests that we can not beat the alloy limit.

**CONCLUSIONS**

This paper examines the thermal conductivity of nanocrystalline composite films using the molecular dynamics computational technique. As expected, a reduced effective thermal conductivity was achieved with an increased interfacial area introduced by the nanocrystal. It was also found that the alloy limit
could not be beat as determined in the comparison of the random crystal and constant atomic fraction of krypton simulations where the minimized effective thermal conductivity was approximately 50% of the solid argon film conductivity. Further work should be done to investigate the difference between interfacial effects parallel versus perpendicular to the transport direction. This work should consider confinement effects introduced by both directions.

REFERENCES


