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Application of elastic wave dispersion relations to estimate thermal properties of nanoscale wires and tubes of varying wall thickness and diameter

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Abstract

This paper reports dependency of specific heat and ballistic thermal conductance on cross-sectional geometry (tube versus rod) and size (i.e., diameter and wall thickness), in free-standing isotropic non-metallic crystalline nanostructures. The analysis is performed using dispersion relations found by numerically solving the Pochhammer-Chree frequency equation for a tube. Estimates for the allowable phonon dispersion relations within the crystal lattice are obtained by modifying the elastic acoustic dispersion relations so as to account for the discrete nature of the material’s crystal lattice. These phonon dispersion relations are then used to evaluate the specific heat and ballistic thermal conductance in the nanostructures as a function of the nanostructure geometry and size. Two major results are revealed in the analysis: increasing the outer diameter of a nanotube while keeping the ratio of the inner to outer tube radius ($\gamma$) fixed increases the total number of available phonon modes capable of thermal population. Secondly, decreasing the wall thickness of a nanotube (i.e., increasing $\gamma$) while keeping its outer diameter fixed, results in a drastic decrease in the available phonon mode density and a reduction in the frequency of the longitudinal and flexural acoustic phonon modes in the nanostructure. The dependency of the nanostructure’s specific heat on temperature indicates 1D, 2D, and 3D geometric phonon confinement regimes. Transition temperatures for each phonon confinement regime are shown to depend on both the nanostructure’s wall thickness and outer radius. Compared to nanowires ($\gamma = 0$), the frequency reduction of acoustic phonon modes in thinner walled nanotubes ($\gamma = 0.96$) is shown to elevate the ballistic thermal conductance of the thin-walled nanotube between 0.2 and 150 K. At 20 K, the ballistic thermal conductance of the thin-walled nanotube ($\gamma = 0.96$) becomes 300% greater than that of a solid nanowire. For temperatures above 150 K, the trend in ballistic thermal conductance inverts. The greater number of phonon modes in nanostructures with increased outer diameter and wall thickness is shown to have a larger contribution to ballistic thermal conductance when compared to the increased contribution from the frequency reduction of acoustic phonon modes in thinner walled nanotubes.

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

1. Introduction

Specific heat and thermal conductivity in bulk crystalline solids are intrinsic properties, which are independent of the crystal dimensions. This is understood to be true even at low temperatures when phonon wavelengths are large. Specific heat and thermal conductivity, however, become dependent on the geometry of the structure when the size of the structure interferes with the existence and propagation of energy...
carriers, predominantly the dominant phonon wavelength in non-metallic materials [1–4].

The mechanisms governing the thermal transport in cylindrical structures are of particular interest in the design and development of more efficient thermal management/heat dissipation technologies [2, 3] and in the design and development of next-generation thermoelectric materials requiring low thermal conductivities combined with high electrical conductance [5]. Undoubtedly, both applications are expected to benefit from further mechanistic studies of thermal transport through cylindrical nanostructures.

Literature is ripe with various methods of thermal conductivity estimates in individual nanowires [3, 4, 6–8], as well as carbon nanotubes [1, 9–12]. However, to date, a direct comprehensive comparison of the specific heat capacity and ballistic thermal conductance in nanowires with those in nanotubes of varying geometry (and dimensions) does not exist. For example, in the past, the thermal properties of carbon nanotubes (CNTs) have been estimated from phonon dispersion relations calculated from spring constant and bond angle models [13]. While such atomistic studies have adequately accounted for diameter dependencies of the CNTs, these models become increasingly complex with the addition of atoms to the wall thickness; the use of 3D cylindrical continuum wave models to represent phonon dispersion is an attractive alternative to investigating the effects of geometry and size on specific heat and ballistic thermal conductance in nanowires and nanotubes. These phonon dispersion relationships provide insights into the allowable phonon frequencies capable of thermal population for a given nanostructure, and are an invaluable comparative tool for understanding the intrinsic differences between the thermal properties of nanoscale wires and tubes.

In the present study, variations in available phonon mode densities as a function of the nanostructure geometry and size are explored using acoustic dispersion relations derived from a continuum-level 3D elastic wave model. Estimates for the allowable phonon dispersion relations are obtained by modifying the elastic dispersion relations so as to account for the discrete nature of the material’s crystal lattice [14]. These phonon dispersion relations are then used to estimate the specific heat and ballistic thermal conductance of the nanostructures. Geometric effects on wave dispersion in cylindrical [15] and rectangular nanowires [16] have previously been studied using continuum-level elastic models. The consequences of these models on phonon dispersion and, therefore, specific heat and ballistic thermal conductance has only been explored in the case of cylindrical nanowires [14]. But, to date, the effects of phonon dispersion modification on specific heat and thermal conductance due to nanotube wall thickness and outer diameter have not been investigated.

2. Modeling

2.1. Elastic dispersion relations as a function of the nanostructure geometry

Dispersion relations are found by numerically solving the Pochhammer-Chree frequency equation for an infinitely long tube. To derive the Pochhammer-Chree frequency equation from the complete 3D cylindrical elastic wave model, we apply the method outlined by Graff [17]. The frequency equation is derived for the nanotube using the assumption of stress-free boundary conditions on both inner and outer free surfaces. However, it must be noted that the stress-free boundary conditions are chosen as a first approximation to analyze the effects of nanoscale geometry on phonon confinement and its effects on specific heat and ballistic thermal conductance. In some recent research [18–20], it has been reported that phonon dispersion is altered by the presence of surface stress and/or residual stress fields within the nanostructures. In this regard, the existence of a positive hoop stress due to bond order loss of surface atoms in solid nanowires is likely to decrease the frequency of the acoustic phonon modes and increase the average phonon group velocity [19]. As will be later shown, these effects are likely to elevate the specific heat as well as the ballistic thermal conductance of the nanostructures. Nonetheless, the role of cross-sectional geometry alone on specific heat and ballistic thermal conductance has not been investigated for nanotubes of varying wall thickness and diameters, and warrants a systematic investigation. For this reason, in the present study, stress-free boundary conditions are chosen to simplify the analysis and at the same time isolate the variables in question.

Due to the complexity of the applied method, it is advantageous to summarize the key points of the derivation. Using a Helmholtz decomposition, the wave displacement field of a cylindrical structure can be described using a scalar potential, \( \phi \), and a vector potential, \( \mathbf{H} \), such that

\[
\mathbf{u} = \nabla \phi + \nabla \times \mathbf{H}.
\]

The potentials \( \phi \) and \( \mathbf{H} \) satisfy the scalar and vector wave equations,

\[
\nabla^2 \phi = \frac{1}{c_1^2} \frac{\partial^2 \phi}{\partial t^2}, \tag{2}
\]

\[
\nabla^2 \mathbf{H} = \frac{1}{c_2^2} \frac{\partial^2 \mathbf{H}}{\partial t^2}, \tag{3}
\]

where \( c_1 \) is the longitudinal (compressive) wave velocity and \( c_2 \) is the transverse (shear) wave velocity, both dependent on the elastic properties of the material

\[
c_1 = \sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}}, \tag{4}
\]

\[
c_2 = \sqrt{\frac{E}{2\rho(1+\nu)}}. \tag{5}
\]

Equations (4) and (5) are formulated in terms the density \( \rho \), Young’s modulus \( E \), and Poisson’s ratio, \( \nu \). For the purpose of this study, \( E = 1.3 \text{ TPa} \) (reflecting the value of Young’s modulus reported for a single-walled CNT in [21]), \( \nu = 0.27 \) and \( \rho = 2260 \text{ kg m}^{-3} \), are used in all calculations.

The scalar components of the displacement vector \( \mathbf{u} \), are described in the cylindrical coordinate system \( r, \theta, \) and \( z \), and are given by

\[
u_r = \frac{\partial \Phi}{\partial r} + \frac{1}{r} \frac{\partial H_z}{\partial \theta} = \frac{\partial H_\theta}{\partial z} \tag{6}
\]
The potentials given in equation (1) have general solutions,

\[ \Phi = f(r) \cos n \theta \cos (\omega t + kz) \]  

\[ H_r = h_r(r) \sin n \theta \sin (\omega t + kz) \]  

\[ H_\theta = h_\theta(r) \cos n \theta \sin (\omega t + kz) \]  

\[ H_z = h_z(r) \cos n \theta \cos (\omega t + kz) \]  

where the functions \( f(r) \), \( h_r(r) \), \( h_\theta(r) \), and \( h_z(r) \) involve solutions to the Bessel equation, such that

\[ f = A Z_n(|\alpha| r) + B W_n(|\alpha| r) \]  

\[ h_3 = A_3 Z_{n+1}(|\beta| r) + B_3 W_{n+1}(|\beta| r) \]  

\[ 2h_1 = h_r - h_\theta = 2A_1 Z_{n+1}(|\beta| r) + 2B_1 W_{n+1}(|\beta| r) \]  

\[ 2h_2 = h_r + h_\theta = 2A_2 Z_n-1(|\beta| r) + 2B_2 W_{n-1}(|\beta| r) \]  

In equations (13)-(16), \( A, B, A_1, B_1, A_2, B_2, A_3, \) and \( B_3 \) are unknown constants, and \( Z_n \) and \( W_n \) represent \( n \)th order ordinary Bessel and modified Bessel functions, respectively. The specifics of Bessel function choice are given in appendix A. \( \alpha \) and \( \beta \) contain the frequency \( \omega \), and the wavenumber \( k \), and are given by

\[ \alpha = \sqrt{\omega^2/c_z^2 - k^2} \]  

\[ \beta = \sqrt{\omega^2/c_r^2 - k^2}. \]  

There are four functions \( f, h_1, h_2, h_3 \) containing the eight unknown constants, and only six boundary conditions that can be applied. The property of gauge invariance [17] allows for any one of \( h_1, h_2, h_3 \) to be equated to zero without loss of generality. Because stress-free boundary conditions are applied to the inner and outer surfaces of the tube, stress field equations are required to determine all the remaining unknown constants.

The stress fields are obtained via the elastic constitutive relation (Hooke’s law),

\[ \sigma_{ij} = \lambda e_{ik} \delta_{ij} + 2\mu e_{ij} \]  

where Lamé’s constant \( \lambda \), and the shear modulus \( \mu \), are functions of \( E \), and \( v \). The components of the strain tensor, \( e_{ij} \), (on the right-side of equation (19)), are given by

\[ e_{rr} = \frac{\partial u_r}{\partial r} \]  

\[ e_{\theta\theta} = \frac{1}{r} \frac{\partial u_\theta}{\partial \theta} + \frac{u_r}{r} \]  

\[ e_{zz} = \frac{\partial u_z}{\partial z} \]  

\[ e_{r\theta} = \frac{1}{2} \left( \frac{\partial u_r}{\partial \theta} + \frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r} \right) \]  

and are determined by differentiation of equations (6)-(8).

Substituting equations (20)-(25) into (19) yields the stress field equations. The stresses \( \sigma_{rr} \), \( \sigma_{rz} \), \( \sigma_{rr} \) are of the only concern and together contain the six unknown constants, \( A_1, B_1, A_2, B_2, A_3, B_3 \), where \( A \) and \( B \) have been eliminated by the application of gauge invariance [17]. The tractions at the inner, \( r = R_i \), and the outer, \( r = R_o \), boundaries are zero and therefore the stress components \( \sigma_{rr} \), \( \sigma_{rz} \), \( \sigma_{rr} \) at the inner and outer boundaries are set to zero.

The Pochhammer-Chree frequency equation is derived by solving a matrix determinant. The elements of the matrix determinant are the coefficients of the six unknown constants \( A_1, B_1, A_2, B_2, A_3, B_3 \) in each of the six stress field equations. Because the unknown constants have nontrivial solutions, setting the six-by-six matrix determinant to zero satisfies the boundary conditions. Solutions to the frequency equation are values of \( k \) and \( \omega \) that satisfy the six-by-six determinant

\[ |c_{ij}| = 0 \quad i, j = 1 \ldots 6. \]  

Components of equation (26) are given in appendix A.

Equation (26) is solved using a bisection algorithm written within MATLAB®. An infinite number of allowable frequency solutions of the type \( \omega(n, m) = f(k) \) are obtained. The \( (n, m) \) solutions are the allowable harmonics or modes of vibration of the structure. Every azimuthal mode number, \( n \), has an infinite number of corresponding radial solutions, \( m \). A total of 50 radial modes, \( m \), are first calculated for each azimuthal mode number, \( n \), for \( n = 0 \ldots 50 \). The class of longitudinal and torsional modes are formed for values of \( n = 0 \). Flexural modes are represented by values of \( n \geq 1 \). Note that all flexural modes must be considered twice due to \( x \) and \( y \) flexural wave polarizations. Normalized frequencies \( (\omega R/\nu_{ij}) \) are calculated for normalized wavenumber \( (kR) \) values from \( kR = 0 \) to \( kR = \pi R/\alpha \), where \( \alpha = 1.7835 \) Å. This choice of the effective lattice constant, \( \alpha \), will be discussed in more detail in section 2.2.

Figure 1 compares the \( n = 0 \) and 1 dispersion curves calculated via equation (26), for a solid rod \((\gamma = 0)\), a thick-walled tube \((\gamma = 0.5)\), and a very thin-walled tube \((\gamma = 0.96)\). Examination of figure 1 reveals the dependency of the allowable wave modes on the cross section geometry. First, a significant decrease in density of the allowable modes of vibration is observed with decreasing tube wall thickness (increasing \( \gamma \)). Secondly, as the outer radius of the tube is increased the density of the available modes of vibrations is observed to increase for all wall thicknesses. Lastly, of the four acoustic modes \((\omega \rightarrow 0 \text{ as } k \rightarrow 0)\), one torsional mode (TA) (figures 1(a), (c) and (e) long dashed), one longitudinal mode (LA) (figures 1(a), (c) and (e) short dashed), and one doubly degenerate flexural mode (FA) (figures 1(b), (d) and (f) short dashed), the normalized frequencies and group velocities.
Figure 1. Elastic dispersion relations calculated by solving equation (26): (a) torsional and longitudinal modes ($n = 0$) of a solid wire ($\gamma = 0$); (b) flexural modes ($n = 1$) of a solid wire ($\gamma = 0$); (c) torsional and longitudinal modes ($n = 0$) of a thick-walled tube ($\gamma = 0.5$); (d) flexural modes ($n = 1$) of a thick-walled tube ($\gamma = 0.5$); (e) torsional and longitudinal modes ($n = 0$) of a thin-walled tube ($\gamma = 0.96$); (f) flexural modes ($n = 1$) of a thin-walled tube ($\gamma = 0.96$). The acoustic modes ($\omega \to 0$ as $k \to 0$) are marked by their respective dashed lines. The normalized frequency of the longitudinal acoustic (LA) mode and the flexural acoustic (FA) mode decrease with decreasing wall thickness (increasing $\gamma$). The slope of the torsional acoustic (TA) mode remains constant. The density of allowable mode vibrations increase with both the increase in wall thickness (decrease in gamma) and the increase in outer radius, $R_o$. 

Figure 2 is a schematic representation of low frequency TA, LA, and FA displacements of a nanotube having a wall thickness characterized by $\gamma = 0.96$ and $R_o = 2.5$ nm. The displacement fields are calculated at a frequency of 1 THz, corresponding to a normalized frequency of $\sim 0.1$. The amplitudes are normalized for a qualitative comparison.
Figure 2. Schematic representation of acoustic mode displacements in $\gamma = 0.96$, 5 nm outer diameter nanotube. (a) Torsional acoustic mode (TA); (b) longitudinal acoustic mode (LA) and (c) doubly degenerate flexural acoustic modes (FA).

Figure 3. Comparison of $n = 0$ longitudinal acoustic (LA) mode dispersion of five structures having a varying ratio of inner to outer diameter, $\gamma$. $\gamma = 0$ is the solid wire, while $\gamma = 0.96$ represents a thin-walled tube. The non-dispersive $\omega = c_1 k$ behavior is shown (dashed line) as a reference.

Figures 3 and 4, respectively, show the variation in the acoustic LA and FA modes as a function of the tube wall thickness. From figure 3 we can infer that all nanostructure geometries studied in the present investigation show a nearly non-dispersive LA mode (similar to $\omega = c_1 k$) for $\omega R_o/c_o < 1.8$ and $k R_o < 1$. These non-dispersive waves exist only for $k R_o < 1$ and are confined to the structure’s longitudinal $z$-axis, since the group velocity of these modes are that of a P-wave, $c_1$ (dashed line). As the wavenumber $k$ is increased, for a fixed outer radius of the nanostructures, the thin-walled tube ($\gamma = 0.96$) shows the maximum deviation from the $c_1$ velocity, followed by structures with increasing wall thickness. This behavior is as expected since the thinnest wall tube has the greatest average circumference, allowing preferential circumferential mode population as the wavelength is decreased (wavenumbers increase). In summary, the LA mode’s transition from non-dispersive to dispersive wave behavior, seen in figure 3 at $k R_o \sim 1$, is indicative of a transition from purely longitudinal wave propagation down the axis of the structure to a coupling of longitudinal waves and azimuthal waves around the structure’s circumference.

The FA mode exhibits a quadratic behavior, $\omega \propto k^2$, for each structure for $k R_o < 1$ (figure 4). This behavior is in agreement with [21–23], and is unlike the linear flexural
dispersion relationship obtained from the graphene zone-folding method for thin-walled tubes [13]. Furthermore, both figures 3 and 4 suggest that at low wavenumbers, all acoustic modes are nearly independent of cross-sectional geometry. This behavior is to be expected, since, at lower frequencies the waves are primarily confined to the longitudinal $z$-axis. For $kR_0 > 1$, the frequency of the LA and FA modes decrease with a reduction in wall thickness as wavenumbers increase past the point for which the wavelengths solely occupy the axial dimension of the tube or rod and transition to a coupled longitudinal and circumferential combined mode (figures 3 and 4).

2.2. Approximating the phonon dispersion relationship

The wavenumbers in the elastic dispersion relation represent waves that vary continuously along the tube axis and are not representative of a periodic Brillouin zone. To better utilize the elastic dispersion model as an approximation for phonon dispersion, the continuum-based frequency spectrum must be modified to account for the discreteness between the discreteness of the crystalline lattice and the continuity of the 3D continuum wave model.

The material used in the description of all nanostructures in this study is assumed to have a diamond lattice. However, it is not possible to choose a conventional unit cell of an interpenetrating face-centered cubic lattice structure so that the unit cell contains one atom per basis [24]. Similar to the work described in [25], an effective lattice constant, $a$, is employed by dividing the conventional unit cell lattice constant of the diamond lattice by one-half. This approximation provides an effective simple cubic lattice with approximately one atom per basis and is appropriate given the perspective of this investigation.

A Born–von-Karman boundary condition is employed to account for the lack of periodicity in the elastic dispersion relation by forcing the group velocity of the lowest frequency $(n, m)$ modes to zero at the far right of the dispersion relation, $k_{\text{max}} = \pi/a$. To apply the Born–von-Karman boundary condition, every $(n, m)$ dispersion mode is multiplied by [14],

$$\sin(ka/2)/(ka/2).$$  \hspace{1cm} (27)

Further discussion regarding equation (27) is provided in appendix B. Figure 5 shows a comparison between a typical elastic dispersion relation (solid lines) derived from the continuum wave model, and the phonon dispersion approximation (dashed lines) obtained by multiplying every $(n, m)$ mode by equation (27). The maximum wavenumber represents the edge of the first Brillouin zone of a symmetric simple cubic lattice. This modification creates an effective standing wave within each lattice cell for the lowest frequency modes, thus allowing the elastic dispersion relations to better approximate the phonon dispersion relation.

The total number of required phonon modes is approximately equal to three times the total number of available lattice points in the cross-sectional area of the tube. The factor of three represents the three available degrees of freedom for each mechanical oscillator. Because the system is approximated as a simple cubic lattice, the total number of $(n, m)$ modes available for thermal population in the cross section of the structure should be three times the number of atoms in the cross-sectional plane. Estimation of the exact number and arrangement of atoms is avoided by limiting the investigation to a temperature domain below 600 K. Since the purpose of this investigation is to examine phonon confinement effects, the maximum value of specific heat is not of interest, and therefore, knowledge of an exact number of phonon modes is not essential. An exact number of phonon modes would be required if complete phonon mode saturation were to take place; this would occur at the maximum value of specific heat. As indicated in figure 6, mode saturation would occur at temperatures greater than 600 K, which is well past the point where specific heat values for each tube geometry would likely converge. Subsequent to the marked $C \propto T^3$ behavior, the short wavelength phonons are unconfined by the dimensions of the structure, and, therefore, temperatures exceeding 600 K are not of interest.

When calculating internal energy and specific heat it is important to have an ample set of phonon modes available for thermal population. As temperature increases the internal energy of the system activates a greater number of phonon modes that are higher in wavenumber and thus frequency. During the present calculations the upper bound of $(n, m)$ is chosen such that the internal energy and thus the specific heat converges to a maximum at the temperature of interest. The
convergence indicates that a proper number of phonon modes have been accounted for in the calculations.

2.3. Internal energy

The volumetric internal energy in the z-direction is calculated by summing the contributions from every \((n, m)\) mode pair.

\[
U(T) = \frac{1}{A_t} \sum_{(n,m)} \int_0^{\pi/a} \frac{\hbar \omega n(m)}{2\pi} \exp(\beta \hbar \omega n(m)) \, dk \approx 1
\]

where \(A_t\) is the cross-sectional area of the nanotube wall thickness, and \(\beta = 1/k_BT\).

The upper bound on the integral in equation (28), \(\pi/a\), is the Debye wave vector cutoff describing the outer edge of the first Brillouin zone in the \(k\)-space. As also inferred from the denominator of the integrand, a surplus of modes beyond the maximum required \((n, m)\) have negligible contribution since the higher order modes are of higher frequency. Therefore, as long as the internal energy converges to a maximum value, a sufficient number of \((n, m)\) modes have been considered.

2.4. Specific heat and ballistic thermal conductance

Differentiating equation (28) with respect to temperature leads to the expression for specific heat capacity per unit volume,

\[
C(T) = \frac{1}{A_t k_BT^2} \sum_{(n,m)} \frac{1}{\pi/a} \int_0^{\pi/a} \frac{\hbar \omega n(m)}{\pi} \exp(\beta \hbar \omega n(m)) \, dk \approx 1
\]

Similar to equation (28), the above expression does not require any externally imposed mode cut-offs due to the temperature dependent nature of the denominator.

The ballistic conductance in the z-direction is the sum of contributions from each \((n, m)\) mode,

\[
g(T) = \sum_{n} \sum_{m} \frac{A_t}{2} C_{n,m} v_{n,m} = \frac{1}{2 k_BT^2} \sum_{n} \sum_{m} \int_0^{\pi/a} \frac{\hbar^2 \omega^2 n(m)}{\pi} \exp(\beta \hbar \omega n(m)) \, dk \approx 1
\]

In equation (30), \(v_{n,m}\) is the group velocity, the slope of the \((n, m)\) dispersion band, at wavenumber \(k\).

When \(\hbar \omega/k_BT \ll 1\), all three integrands in equations (28)–(30) have appreciable contributions to the value of their respective integrals. Therefore, phonon frequencies satisfying

\[
\omega \ll k_BT/h \tag{31}
\]

are the most significant contributors to the internal energy, specific heat, and the ballistic thermal conductance [26]. Most importantly, equation (31) provides the criteria for thermal mode activation.

Equations (29)–(31) reveal that specific heat and ballistic thermal conductance are primarily controlled by three phonon mode characteristics within a typical nanostructure. First, of all the allowable phonon modes, the lowest frequency phonon modes are the first to thermally populate with increasing temperature. Secondly, lower frequency phonon modes are the greatest contributors to internal energy, specific heat, and the ballistic thermal conductance. Lastly, the total thermal contribution is the sum of all the thermally activated phonons at a particular temperature.

3. Results and discussion

Qualitatively, geometric phonon confinement effects can be explained in terms of the dominant phonon wavelength of the system [1]. The dependence of the dominant phonon wavelength, \(\lambda_d\) on temperature is given by [26],

\[
\lambda_d \approx 2\pi c_{avg}/k_BT \tag{32}
\]

where \(c_{avg}\) is an averaged phonon group velocity, which can be calculated from any one or group of \((n, m)\) modes for any range wavenumbers from 0 to \(\pi/a\). Decreasing the temperature of the system drives the dominant phonon wavelength of the system higher. Lower temperatures will eventually cause the wall thickness and circumferential dimensions of the nanotube to become ‘frozen-out’ as the dominant phonon wavelength exceeds the respective characteristic length of the dimension. Similar to the elastic waves, larger phonon wavelengths (smaller wavenumbers) are confined to the length of the tube, giving rise to the 1D regime. As temperatures increase, the dominant phonon wavelength becomes smaller and begins to occupy the next smaller dimensions of the system, starting with the circumferential length (2D regime), and followed by the radial dimensions,
i.e., the wall thickness or the diameter. Phonon population of the wall thickness marks the 3D regime. Once this occurs, with regards to phonon confinement, the structure is thermally analogous to its bulk material.

3.1. Tube thickness variation

Figure 6 shows the specific heat capacities (per unit volume) for five cylindrical geometries. As expected, with an increase in the wall thickness the thermal behavior converges onto that of a solid nanowire. Evidence of 1D → 2D → 3D transitional behavior is apparent with increasing temperature (figure 6).

In the low temperature limit, according to equation (31), acoustic phonon modes contribute significantly to equations (29) and (30). In the case of nanowires, the acoustic dispersion relations have been approximated with analytic forms for LA ($\omega = c_1 k$), TA ($\omega = c_2 k$), and FA ($\omega = c_D k^2$) modes, where $c_o = \sqrt{E/\rho}$ and $D$ is the diameter of the nanowire [14]. Contributions to specific heat from each aforementioned phonon mode can be independently found using equation (29). At low temperatures, the LA and TA phonon mode contributions to specific heat exhibit a $C \propto T$ behavior, while the FA phonon mode contribution shows a $C \propto T^{0.5}$ behavior [14]. In this study, FA phonon mode dominance in the low temperature limit is present for all geometries and shown by a $C \propto T^{0.5}$ behavior (figure 6). FA mode dominance is justified since the quadratic mode behaviors (figure 4 inset) are of lower frequency, and thus are higher contributing when the nanotube (at 600 K) are incapable of thermal activation $\gamma \approx 1.67$ nm. Because the phonon behavior in a bulk crystal. The 3D specific heat of a nanowire at elevated temperatures is derived by substituting the aforementioned bulk phonon relations into equation (29).

The results of the present study suggest that the temperature at which the transition from 2D to 3D behavior occurs is dependent on the wall thickness of the nanotubes. Figure 6 shows that for each of the nanotube geometries investigated, except for the case of the thinnest wall tube ($\gamma = 0.96$), the specific heat converges to the $T^3$ behavior of the nanowire. Interestingly, the $\gamma = 0.96$ nanotube is observed to be exempt from the $T^3$ transition. At 600 K the dominant phonon wavelength, $\lambda_4$, is estimated using equation (32) to be approximately 1.67 nm. Because the $\gamma = 0.96$ nanotube has a 1 Å wall thickness, the phonons in the radial dimension of the nanotube (at 600 K) are incapable of thermal activation because their wavelengths are larger than the wall thickness of the tube.

Figure 7 shows the calculated ballistic conductance of cylindrical geometries $\gamma = 0, 0.5, 0.75, 0.9, \text{and} 0.96$ normalized by the value of quantum conductance $g_o = \pi k_B^2 T / 6 h$ [28]. These geometries correspond to wall thicknesses of a solid nanowire, 1.25 nm, 0.625 nm, 0.25 nm and 1 Å, respectively. The similarity in conductance at low temperatures confirms that the same transport mechanisms exist in nanowires and nanotubes regardless of wall thickness. Figures 3 and 4 verify that each structure’s geometry supports comparable mode vibrations at low frequencies. Therefore, the low temperature thermal behavior of nanowires and nanotubes are conclusively identical.

According to figure 7, at temperatures between 0.3 and 150 K, ballistic conductance is seen to increase with decreasing wall thickness. At 20 K, the thermal conductance of the thinnest walled tube ($\gamma = 0.96$) is 300% greater than that of the solid nanowire ($\gamma = 0$). Reducing the nanotube wall thickness decreases the frequency of the LA and FA phonon modes, thereby increasing the integrand of equation (29), and increasing the value of thermal conductance. Interestingly, as the temperature increases past 150 K, the trend in conductance changes. At 300 K, the ballistic thermal conductance of the thinnest walled nanotube shows a 50% decrease compared to the solid nanowire (figure 7). Plausibly, because the number of thermally populated phonon modes increases with increasing temperature (via equation (30)). It is possible.
that the temperature, above 150 K, is high enough so that the effect of the increased number of contributing phonon modes supersedes the effect of the highly contributing lower frequency phonon modes which were understood to play a dominant role at lower temperatures.

3.2. Outer diameter variations

Figure 8 shows the calculated specific heat for a thick-walled nanotube ($\gamma = 0.5$) as a function of outer diameter. Specific heat is shown to decrease with increasing outer diameters at low temperatures. This reduction of specific heat in nanotubes with increasing outer diameter follows a trend similar to those observed in nanowires [14, 25].

With increasing temperatures, larger diameter nanotubes having the same value of $\gamma$ are first to deviate from a 1D specific heat regime (figure 8). A similar phenomenon is seen by increasing $\gamma$ for a nanotube having a fixed outer diameter (figure 6). These results suggest that increasing the outer diameter of a fixed $\gamma$ nanotube is mechanistically similar to keeping the outer diameter of the tube fixed and decreasing the wall thickness. In both cases, the mean circumference of the nanostructure increases. As previously discussed in the case of the elastic dispersion curves (section 2.1), a cylindrical nanostructure with an increased mean circumference is more apt to coupled longitudinal and circumferential phonon population with increasing temperatures, and will therefore be the first structure to enter a 2D phonon confinement regime.

Figure 9 indicates that increasing the diameter of a nanotube with fixed $\gamma$ increases its ballistic thermal conductance. When compared to small outer diameter nanotubes, the larger 20 nm outer diameter nanotube with the same value of $\gamma$ ($\gamma = 0.5$) begins to show elevated thermal conductance values, at approximately 2 K. An approximate one order of magnitude increase in thermal conductance between the 20 nm outer diameter nanotube and the 5 nm outer diameter nanotube is observed at 200 K. The inversion of the temperature trend in conductance shown in figure 7 is not present in figure 9. According to figure 1, increasing the outer radius of the nanostructure creates a greater number of available $(n, m)$ phonon modes within a set frequency range for a fixed value of $\gamma$ ($\gamma = 0.5$). Thereby, increased temperatures increase the number of contributing phonon modes and provide a greater number of $(n, m)$ contributions to the summations in equations (28)–(30). This explains the elevation in thermal conductance with temperature for the larger radius nanotubes.

It is worth discussing the absence of a trend inversion in ballistic conductance in figure 9, which is present in figure 7. Unlike $\gamma$ variations, changing $R_o$ does not alter the phonon group velocities within the nanostructure, or lower the available $(n, m)$ phonon frequencies. According to equation (31), of the few thermally populated phonons in the thin-walled structure, the lower frequency acoustic phonons have a higher contribution to internal energy when compared to the acoustic phonons in the relatively thick-walled nanostructures. Therefore, thinner walled nanostructures of the same outer diameter are shown to have a higher conductance between 2 and 150 K. As temperature increases, the lower frequency phonons, which have a greater energy contribution per mode, must compete with the sum contribution from the growing number of total $(n, m)$ phonon modes, which, although having less contribution per mode, are more numerous in thicker walled nanostructures. Because increasing $R_o$ does not lower the frequency of available phonons, the contribution of each phonon to the nanostructure’s thermal conductance remains the same, therefore, variations in $R_o$...
The conductance is normalized by the quantum of thermal conductance, $g_e = \pi^2 k_B^2 T / 3h$ [28]. Conductance values converge to $4g_e$ at low temperatures due to contributions from the four acoustic modes, while maintaining a fixed value of $\gamma$ (figure 9) do not produce the trend inversion seen in figure 7.

4. Summary

Complete dispersion relations obtained from solving the Pochhammer-Chree frequency equation are shown to be a useful tool for investigating the thermal property dependence on geometry and size of elastic non-metallic crystalline nanotubes. While past literature has extensively evaluated 1D to 3D transitions in nanowires with temperature, this work captures similar trends in cylindrical nanotubes with varying geometry. The results of the study suggest that at low temperatures similar thermal transport mechanisms exist in nanowires and/or nanotubes regardless of their wall thickness or outer diameter. Elastic dispersion relations confirm each structure’s capability to support comparable low frequency/low wavenumber modes. The transitions unique to nanotubes in the mid-temperature range are found to be dependent on geometry, and exhibit an initial $T^{1.5}$ dominance evolving towards bulk- $T^3$ behavior as the temperature is increased. An elevation in the thermal conductance of thin-walled nanotubes, compared to the same size outer diameter nanowire, is possible between 2 and 150 K, and is attributed to the reduction in the frequency of acoustic phonon modes. At room temperature, the same thin-walled nanotube shows a decrease in ballistic thermal conductance when compared to the nanowire comprised of the same material.

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Appendix A

\[
\begin{align*}
    c_{11} &= [2n(n-1)- (b^2-k^2)a^2] Z_n(\alpha_1 a) + 2\lambda_1 \alpha_1 a Z_{n+1}(\alpha_1 a), \\
    c_{12} &= 2k_1 b^2 Z_n(\beta_1 a) - 2ka(n+1) Z_{n+1}(\beta_1 a), \\
    c_{13} &= -2n(n-1) Z_n(\beta_1 a) + 2\lambda_2 n_1 b Z_{n+1}(\beta_1 a), \\
    c_{14} &= [2n(n-1)- (b^1_1-k^2)a^2] W_n(\alpha_1 a) + 2\alpha_1 a W_{n+1}(\beta_1 a), \\
    c_{15} &= 2\lambda_2 k_1 b^2 W_n(\beta_1 a) - 2(n+1)ka W_{n+1}(\beta_1 a), \\
    c_{16} &= -2n(n-1) W_n(\beta_1 a) + 2n_1 b W_{n+1}(\beta_1 a), \\
    c_{21} &= 2(n(n-1) Z_n(\alpha_1 a) - 2\lambda_1 n_1 a Z_{n+1}(\alpha_1 a), \\
    c_{22} &= -2k_1 b^2 Z_n(\beta_1 a) + 2ka(n+1) Z_{n+1}(\beta_1 a), \\
    c_{23} &= -[2n(n-1) - b^2 Z_n(\beta_1 a) - 2\lambda_2 b_1 Z_{n+1}(\beta_1 a), \\
    c_{24} &= 2n(n-1) W_n(\alpha_1 a) - 2n_1 a W_{n+1}(\alpha_1 a), \\
    c_{25} &= -2\lambda_2 k_1 b^2 W_n(\beta_1 a) + 2ka(n+1) W_{n+1}(\beta_1 a), \\
    c_{26} &= -[2(n(n-1) - n Z_n(\beta_1 a) - 2\lambda_2 n_1 a Z_{n+1}(\beta_1 a), \\
    c_{31} &= 2n_1 a Z_{n+1}(\alpha_1 a), \\
    c_{32} &= 2\lambda_2 n_1 b Z_{n+1}(\alpha_1 a), \\
    c_{33} &= -2n_1 a Z_{n+1}(\alpha_1 a), \\
    c_{34} &= 2n_1 a W_{n+1}(\alpha_1 a) - 2\lambda_1 n_1 a Z_{n+1}(\alpha_1 a), \\
    c_{35} &= -2\lambda_1 n_1 b W_{n+1}(\alpha_1 a) + (b^2-k^2)a^2 W_{n+1}(\beta_1 a), \\
    c_{36} &= -2\lambda_1 n_1 b W_{n+1}(\alpha_1 a), \\
    c_{41} &= [2(n(n-1) - (b^2-k^2)b^2 Z_n(\alpha_1 b) + 2\lambda_1 a_1 b Z_{n+1}(\alpha_1 b), \\
    c_{42} &= 2k_1 b^2 Z_n(\beta_1 b) - 2kb(n+1) Z_{n+1}(\beta_1 b), \\
    c_{43} &= -2(n(n-1) Z_n(\beta_1 b) + 2\lambda_2 n_1 b Z_{n+1}(\beta_1 b), \\
    c_{44} &= [2(n(n-1) - (b^1_1-k^2)b^2] W_n(\alpha_1 b) + 2\alpha_1 b W_{n+1}(\alpha_1 b), \\
    c_{45} &= 2\lambda_2 k_1 b^2 W_n(\beta_1 b) - 2(n+1)kb W_{n+1}(\beta_1 b), \\
    c_{46} &= -2(n(n-1) W_n(\beta_1 b) + 2n_1 b W_{n+1}(\beta_1 b), \\
    c_{51} &= 2n(n-1) Z_n(\alpha_1 b) - 2\lambda_1 n_1 a Z_{n+1}(\alpha_1 b), \\
    c_{52} &= -2k_1 b^2 Z_n(\beta_1 b) + 2kb(n+1) Z_{n+1}(\beta_1 b), \\
    c_{53} &= -[2(n(n-1) - b^2 Z_n(\beta_1 b) - 2\lambda_2 b_1 Z_{n+1}(\beta_1 b), \\
    c_{54} &= 2n(n-1) W_n(\alpha_1 b) - 2\alpha_1 b W_{n+1}(\alpha_1 b), \\
    c_{55} &= -2\lambda_2 k_1 b^2 W_n(\beta_1 b) + 2kb(n+1) W_{n+1}(\beta_1 b), \\
    c_{56} &= -[2(n(n-1) - \beta^2 Z_n(\beta_1 b) - 2\beta_1 b W_{n+1}(\beta_1 b), \\
    c_{61} &= 2n_1 a Z_{n+1}(\alpha_1 b) - 2\lambda_1 n_1 a Z_{n+1}(\alpha_1 b), \\
    c_{62} &= 2n_1 b Z_{n+1}(\alpha_1 b) - (b^2-k^2)b^2 Z_{n+1}(\beta_1 b), \\
    c_{63} &= -nkb Z_{n}(\beta_1 b), \\
    c_{64} &= 2nkb W_{n}(\alpha_1 b) - 2\alpha_1 b W_{n+1}(\alpha_1 b), \\
    c_{65} &= -2\lambda_1 n_1 b W_{n+1}(\beta_1 b) - (b^2-k^2)b^2 W_{n+1}(\beta_1 b), \\
    c_{66} &= -nkb W_{n}(\beta_1 b),
\end{align*}
\]
where \( a = R_0 \) and \( b = R_1 \). If \( \alpha^2 \) or \( \beta^2 \) is greater than zero, \( Z_\alpha \) is the \( n \)th order Bessel Function of the first kind \( J_\alpha \). If \( \alpha^2 \) or \( \beta^2 \) is less than zero, \( Z_\beta \) corresponds to the modified Bessel function of the first kind \( I_\beta \). Similarly, \( W_\alpha \) corresponds to the Bessel function of the second kind, \( Y_\alpha \), or modified Bessel function of the second kind, \( K_\alpha \), depending on the sign of \( \alpha^2 \) or \( \beta^2 \). The constants \( \lambda_1 \), and \( \lambda_2 \) are \(+1\) if Bessel functions \( J \) and \( Y \) are used, and \(-1\) if \( I \) and \( K \) are used. The reader is referred to [17], for further specifics regarding the derivation of the elastic frequency equation.

**Appendix B**

Equation (27) is designed to force the group velocity of only the acoustic modes (\( m = 1 \) for \( n = 0 \) and 1) to zero at maximum wavenumber. While not designed to do so, the group velocity of modes \( m = 2 \) and 3 for \( n = 0 \) and 1 are near zero. For \( m > 3 \) for \( n = 0 \) and 1, and for all \( m \) modes belonging to \( n > 1 \), modification of the elastic dispersion relation using equation (27) causes slightly negative group velocities at maximum wavenumber, especially for higher frequency modes. This has been found to be a mathematical artifact having no physical meaning. Using equation (31) and considering the temperature domain of interest, 0.1–600 K, the highest thermally contributing frequencies of the dispersion curve may be estimated as those frequencies below 71 THz. Therefore, using the modification term creates an effective “Born–von-Karman” boundary condition at \( k_{\text{max}} \) in the modes that contribute most to specific heat and thermal conductance and is therefore a better approximation for phonon dispersion than the elastic dispersion curves. While the calculation of thermal conductivity would require further estimation of phonon scattering effects and is therefore beyond the scope of this investigation, it is unsurprisingly a natural extension of the current findings. It has been suggested in the literature that using the elastic dispersion relations without further modification would only affect thermal conductivity calculations by less than 10% [29].

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