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Approximate Analytical Models for Phonon Specific Heat and Ballistic Thermal Conductance of Nanowires

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ABSTRACT

We introduce simple approximate analytical models for phonon specific heat and ballistic thermal conductance of nanowires. The analytical model is in excellent agreement with the detailed numerical calculations based on the solution of the elastic wave equation and is also in good agreement with the ballistic thermal conductance data by Schwab et al. (*Nature* 2000, *404*, 974). Finally, we propose a demarcating criterion in terms of temperature, dimension, and material properties to capture the dimensional crossover from a three-dimensional (3D) bulk system to a one-dimensional (1D) system.

Study of thermal properties of nanowire systems is important both for fundamental understanding of the underlying physics in low-dimensional system and for applications such as high *ZT* thermoelectric materials. Recent years have seen significant advancement in both experimental[1−3] and theoretical[4−7] studies of thermal transport in nanowires. Thermal transport due to phonons in nanowires can be divided into several regimes. One such regime is where the mean free path (mfp) of phonons is larger than both the diameter and the length of the nanowire. In this regime, thermal transport due to phonons is ballistic. In this ballistic transport regime, there is a subregime where the dominant wavelength (λ_d) of phonons is comparable to or larger than the diameter (d) of the nanowire leading to phonon confinement effects.[2,3,6,7] In the limit of $\lambda_d \gg d$, the ballistic thermal conductance reduces to the universal quantum of thermal conductance,[3,6,7] $g_0 = \pi k_b^2 T/6\hbar$ where k_b is the Boltzmann constant, $\hbar$ is the reduced Planck constant, and T is the temperature.

Experimental demonstration of g_0 by Schwab et al.[3] has generated a lot of interest on the effect of phonon confinement on thermal conductance in the research community. This is interesting for both the understanding of the underlying physics and exploring these concepts for practical applications, such as enhancement of thermal conductance using phonon waveguides. Modeling of thermal transport in nanowires covering the bulk limit and the quantized limit is done in the literature by numerical simulations,[6,8,9] which require time-consuming efforts and do not convey much information regarding the importance of various geometrical and material parameters. In this paper, we introduce a simple analytical formula for ballistic thermal conductance of nanowires. The analytical formula covers both the dimensional-reduced and bulk range and clearly captures the dimensional crossover from one dimension (1D) to three dimensions (3D). The conductance given by this simple formula is in excellent agreement with the numerical simulation and also with the experimental data by Schwab et al.[3] The model incorporates all the relevant material parameters and the size of the nanowire, thereby making it applicable to general cases. We also define a demarcating criterion to show when phonon confinement effects are important. This criterion depends on the temperature, diameter, and material properties of the nanowire and can be used for quick assessment regarding the importance of phonon confinement effects.

On the other hand, the specific heat (heat capacity per unit volume) is a more fundamental material property at thermal equilibrium. Specific heat of carbon nanotubes[10] and other nanotube systems[11] has been studied extensively both experimentally and theoretically. Despite the significant potential for various applications, studies on specific heat of nanowire systems have been very rare. To the best of our knowledge, no experimental work has been reported on the specific heat of nanowires so far. Here, we calculate the specific heat of nanowires by exactly solving the elastic wave

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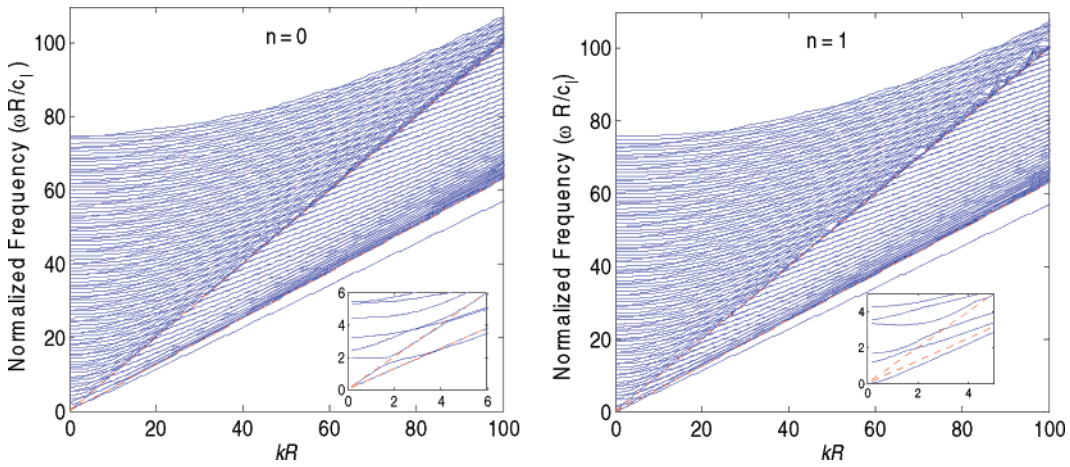

Figure 1. Representative dispersion relations of a circular rod for for $n = 0$ and $n = 1$. Insets show the magnified regions for small values of ω and k.

equation in the nanowire. Similar to the conductance, we introduce an analytical model for the specific heat. The analytical model is in excellent agreement with the exact calculations. Analogous to the conductance, we again define a demarcating criterion and show when phonon confinement effects become important for specific heat.

Phonon confinement effects are important at low temperatures because λ_d can become comparable to the diameter of the nanowire at low temperatures. Generally, λ_d of thermally excited phonons can be estimated by[2] $\hbar\omega_d = 2\pi\hbar c/\lambda_d \approx 2.82k_bT$, where c is the sound velocity and ω_d is the dominant phonon frequency. This relation shows that λ_d is inversely proportional to temperature. At very low temperatures, λ_d can be large; for example, $\lambda_d \sim 6$ nm at $T = 10$ K for silicon. This shows that phonon confinement effects will be important at low temperatures. Therefore, the calculations have been performed for low temperatures, that is, $T \ll \theta_D$, where θ_D is the Debye temperature. Since $T \ll \theta_D$, the continuum elastic wave equation is a good approximation to the full lattice dynamic calculations and can be used for calculating the thermal properties.[13]

Normal modes of wave transport through a waveguide can be solved by solving the elastic wave equation;[9,12] however, various limiting solutions can be obtained without solving the full elastic equation. When the wavelength of acoustic wave is much larger than the diameter of a nanowire, the wire behaves like a 1D bar. In this regime, there are four fundamental modes of vibrations, that is, $\omega = 0$ at $k = 0$: one longitudinal, one torsional, and two flexural modes. k is the wavevector along the axial direction of the wire. The velocity of phonons for the longitudinal mode is given by $c_{L,W} = \sqrt{E/\rho}$, where E is the Young's modulus and ρ is the mass density. The velocity of the torsional mode is given by $v_{T,W} = \sqrt{\mu/\rho}$ where μ is the shear modulus. The flexural modes follow a quadratic dispersion relation[12] $\omega = c_{L,W}k^2R/2$, where R is the radius of the nanowire and k is the wave vector along the wire direction. The heat capacity per unit volume for a one-dimensional system corresponding to each mode for $T \ll \theta_D$ can be expressed as

$$C_{1D} = \frac{1}{A}\frac{\partial}{\partial T}\int_0^\infty \frac{dk}{2\pi}\frac{\hbar\omega(k)}{\exp[\beta\hbar\omega(k)] - 1} \quad (1)$$

where A is the cross-sectional area of the wire, k is the wave vector, and $\beta \equiv 1/k_bT$. The total specific heat of the longitudinal, torsional, and the flexural modes from eq 1 can be shown to be

$$C_{1D} = \frac{\pi k_b{}^2 T}{3\hbar A}\left(\frac{1}{c_{L,W}} + \frac{1}{c_{T,W}}\right) + \frac{3.472T^{1/2}}{\pi A}\sqrt{\frac{2k_b{}^3}{\hbar c_{L,W}R}} \quad (2)$$

Equation 2 indicates that C_{1D} varies as $T^{1/2}$ at very low temperatures and varies as T at relatively higher temperatures. The $T^{1/2}$ dependence term is due to the contribution of the flexural modes whose dispersion dependence is quadratic.

The ballistic thermal conductance contributed by the four fundamental modes for a 1D system for perfect transmission condition is given by[3,6] $g_{1D} = 4g_0$.

In the other limit where the wavelength of the acoustic waves is much smaller than the diameter of the wire, then the wire behaves like a 3D bulk solid.[12] For a bulk elastic body, there are three modes: one longitudinal and two transverse modes. The velocity of the longitudinal mode is $c_{L,B} = \sqrt{(\lambda+2\mu)/\rho}$, where λ and μ are the elastic Lamé's constants. The velocity of the transverse modes is given by $c_{T,B} = \sqrt{\mu/\rho}$. For $T \ll \theta_D$, the specific heat of a bulk 3D solid is[13]

$$C_{3D} = 4\pi^2/30 \times (k_b{}^4/\hbar^3)(c_{L,B}{}^{-3} + 2c_{T,B}{}^{-3})T^3 \quad (3)$$

The ballistic thermal conductance for $T \ll \theta_D$ is given by[14]

$$g_{3D} = A \times \pi^2/30 \times (k_b{}^4/\hbar^3)(c_{L,B}{}^{-2} + 2c_{T,B}{}^{-2})T^3 \quad (4)$$

In the intermediate regime between the 1D and 3D behavior, the elastic wave equation needs to be solved with a traction-free boundary condition at the surface of the

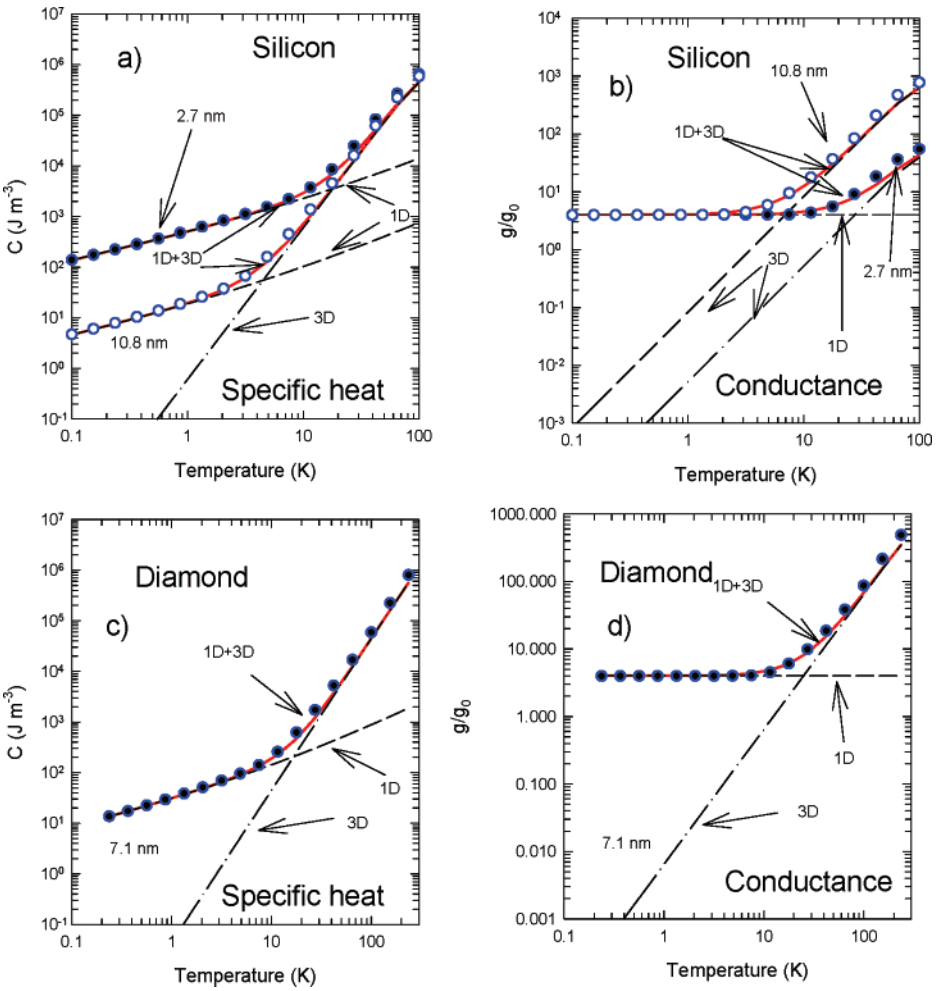

Figure 2. Specific heat and ballistic conductance of Si and diamond nanowires. Symbols are the calculations based on detailed numerical simulation by solving the elastic wave equations. The lines going through the symbols are the proposed approximation for C (eq 7) and g (eq 8). Figures show that the proposed approximation is in excellent agreement with the detailed numerical calculations.

nanowire.[6,7,9] We have used the formulations outlined in Graff[12] to solve for the dispersion relation in the nanowire. For example, the dispersion results for Si are representatively shown in Figure 1. In Figure 1, the wavevector and frequency are expressed in dimensionless groups as kR and $\omega R/c_L$, respectively. For the vibration of a circular wire, each normal vibrational mode can be decomposed into the axial mode (characterized by k) and transverse mode, characterized by a azimuthal mode number n and a radial mode number m. For $n = 0$ modes, there are two fundamental modes ($\omega = 0$ at $k = 0$). These correspond to the longitudinal and torsional modes of the wire. For $n = 1$ modes, the only fundamental modes are the two flexural modes (the two flexural modes of different polarity coincide with each other).

The specific heat for all the modes is given by summing the contribution from all the normal modes,

$$C(T) = \frac{1}{\pi k_b T^2 A} \sum_s \int_{\omega_0}^{\omega_{max}} \left(\frac{dk}{d\omega}\right) \frac{\hbar^2 \omega_{s,k}^2 \exp(\beta\hbar\omega_{s,k})}{[\exp(\beta\hbar\omega_{s,k}) - 1]^2} d\omega \qquad (5)$$

where s signifies the transverse mode numbers (n,m) and A is the cross-sectional area of the wire. Similarly, the total ballistic conductance due to all the normal modes is

$$g = \frac{1}{2\pi k_b T^2} \sum_s \int_{\omega_0}^{\omega_{max}} \left(\frac{dk}{d\omega}\right) \frac{\hbar^2 \omega_{s,k}^2 \exp(\beta\hbar\omega_{s,k})}{[\exp(\beta\hbar\omega_{s,k}) - 1]^2} v_{g,s}\, d\omega$$
$$= \frac{1}{2\pi k_b T^2} \sum_s \int_{\omega_0}^{\omega_{max}} \frac{\hbar^2 \omega_{s,k}^2 \exp(\beta\hbar\omega_{s,k})}{[\exp(\beta\hbar\omega_{s,k}) - 1]^2} d\omega \qquad (6)$$

Figure 2 shows the results for Si and diamond nanowires as functions of temperature. Figure 2 shows that both C and g reduce to the limiting values; that is, at low temperatures, they reduce to the value of a 1D system, and at higher temperatures, they reduce to the values of a 3D system.

Obtaining the phonon dispersion relations from elastic wave equation to evaluate eqs 6 and 7 is time-consuming and tedious. Furthermore, numerical evaluation does not provide much information regarding which parameters are more important and cannot be used for quick assessments. Therefore, we propose an approximate analytical model for both C and g to capture the transitional regime from 1D to 3D behavior. The approximation is based on the result that

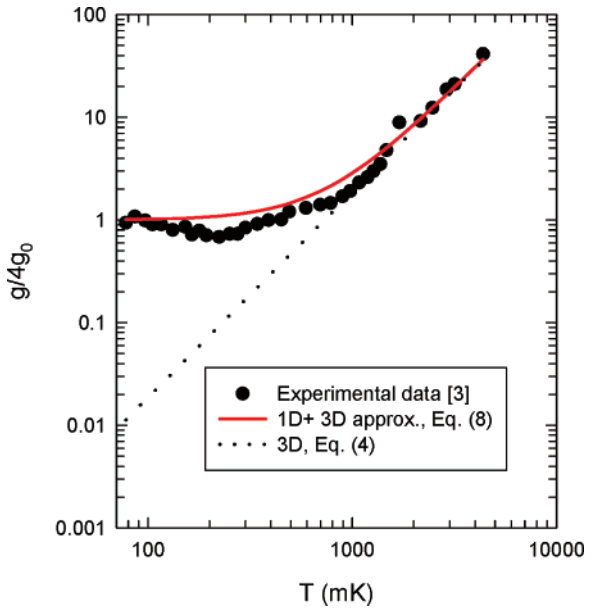

Figure 3. Comparison with experimental data of Schwab et al.[3]

for low temperatures, both C and g reduce to their 1D values, whereas at higher temperatures, they reduce to their 3D values. Therefore, we propose that C and g can be effectively written as $C = C_{1D} + C_{3D}$ and $g = g_{1D} + g_{3D} = 4g_0 + g_{3D}$. By approximating C and g like this, we expect that it will reduce to the limiting values and will also accurately capture the transitional regime. Therefore,

$$C = \frac{\pi k_b^2 T}{3\hbar A}(c_{L,W}^{-1} + c_{T,W}^{-1}) + \frac{3.472T^{1/2}}{\pi A}\sqrt{\frac{2k_b^3}{\hbar c_{L,W} R}} + 4\pi^2/30 \times (k_b^4/\hbar^3)(c_{L,B}^{-3} + 2c_{T,B}^{-3})T^3 \quad (7)$$

$$g = 4\pi k_B^2 T/6\hbar + A \times \pi^2/30 \times (k_b^4/\hbar^3)(c_{L,B}^{-2} + 2c_{T,B}^{-2})T^3 \quad (8)$$

Figure 2 shows the comparison of eqs 7 and 8 with the detailed calculation based on eqs 5 and 6. Figure 2 shows that the eqs 7 and 8 match very well with the exact calculations. Figure 3 shows the comparison between the data of ballistic conductance by Schwab et al.[3] and eq 8. For the area (A) in eq 8, the minimum area of the catenoidal nanomembrance (60 nm × 200 nm) is taken.[14] Figure 3 shows that the proposed approximate model matches well with the data.

Finally, we propose a demarcating criterion for transition from 1D to 3D behavior. The criterion can be defined by equating the 1D and 3D values of C and g. For C, the flexural contribution is important only at very low T, that is, for $T \rightarrow 0$ because $C \propto T^{1/2}$, whereas transition to 1D to 3D takes place at slightly higher temperatures. Therefore, while equating 1D and 3D specific heat, flexural mode contribution can be neglected. By equating the 1D and 3D values, the transition criteria for C and g, respectively, can be obtained as

$$\pi k_b^2 T(c_{L,W}^{-1} + c_{T,W}^{-1})(3\hbar A)^{-1} = 4\pi^2/30 \times (k_b^4/\hbar^3)(c_{L,B}^{-3} + 2c_{T,B}^{-3})T^3 \quad (9)$$

$$4\pi k_B^2 T/6\hbar = A \times \pi^2/30 \times (k_b^4/\hbar^3)(c_{L,B}^{-2} + 2c_{T,B}^{-2})T^3 \quad (10)$$

For a circular nanowire assuming that $c \sim c_D$ (Debye velocity), eqs 9 and 10 give

$$T_{cross\_C} \approx \frac{\sqrt{10}\,\hbar c_D}{\pi k_B d} \quad (11)$$

$$T_{cross\_g} \approx \frac{2\sqrt{5}\,\hbar c_D}{\pi k_B d} \quad (12)$$

where d is the diameter of the wire. From eqs 11 and 12, one can clearly see that the transition temperatures for the specific heat and the ballistic conductance are the same up to a constant ratio of $\sqrt{2}$. The transition temperature depends only on $c_D d^{-1}$. Plugging in the physical constants, $T_{cross\_C} = 7.68 \times 10^{-12} c_D d^{-1}$ and $T_{cross\_g} = 10.88 \times 10^{-12} c_D d^{-1}$. For Si nanowires of diameters 2.7 and 10.8 nm, T_{cross_g} is roughly 24.1 and 6.4 K, respectively. For diamond nanowire of diameter 7.1 nm, T_{cross_g} is 21.5 K. Figure 2 shows that crossover takes place around these temperatures. Therefore, phonon confinement is significant only around and below these temperatures.

In summary, we have introduced a very simple analytical model to capture the effects of phonon confinement on specific heat and ballistic thermal conductance of nanowires. The model is in excellent agreement with detailed numerical simulation and experimental data. Results show that phonon confinement effects are important at very low temperatures. A demarcating criterion for transition from 1D to 3D behavior was also proposed.

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