Nanoscale heat transfer and thermal-electric energy conversion[*]

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Abstract. Experimental and theoretical studies in recent years have shown that heat transfer in nanostructures differs significantly from in macrostructures. This paper summarizes some of the past experimental and modeling work and our current understanding of the heat conduction mechanisms in nanostructures. Applications of the nanoscale heat conduction phenomena in energy conversion and photothermal spectroscopy are discussed.

1. INTRODUCTION

Modern technology has enabled the fabrication of materials and devices with characteristic dimensions of a few nanometers. Examples are superlattices, nanowires, and quantum dots. At these length scales, the familiar continuum Fourier law for heat conduction is expected to fail due to both classical and quantum size effects [1-4]. This paper summarizes some past work and the current understanding of heat conduction in nanostructures. Section 2 gives a brief overview on the fundamental physics that distinguishes phonon heat conduction in nanostructures from that in macrostructures. Section 3 discusses a few examples of size effects in nanostructures. Potential applications of nanoscale heat conduction phenomena, particularly in the area of energy conversion, are discussed in Sect. 4.

2. FUNDAMENTAL PHYSICS

Heat conduction in dielectric materials and most semiconductors is dominated by phonons. Size effects appear if the structure characteristic length is comparable to or smaller than the phonon characteristic lengths. Two kinds of size effects can exist: the classical size effect, when phonons can be treated as particles, and the wave effect, when the phonon wave phase information becomes important. Distinction between these two regimes depends on several characteristic lengths, which we discuss below.

2.1 Characteristic lengths

The important characteristic lengths of phonon heat conduction are the mean free path, the wavelength, and the phase coherence length [5]. The mean free path is the average distance that phonons travel between successive collisions. The mean free path Λ is often estimated from kinetic theory:

$$k = \frac{1}{3} \int_0^{\omega_{max}} C_\omega v_\omega^2 \tau_\omega d\omega = \frac{\Lambda}{3} \int_0^{\omega_{max}} C_\omega v_\omega d\omega \tag{1}$$

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where C_ω, v_ω, and τ_ω are the volumetric specific heat, the velocity, and the relaxation time at each phonon frequency, respectively. In silicon, for example, the phonon mean free path is on the order of ~300 nm [1,6].

The phase of a wave can be destroyed during collision, which is typically the case in inelastic scattering processes, such as the phonon-phonon collision. If the phase destroying scattering process occurs frequently inside the medium, the wave characteristic of carriers can be ignored and the transport falls into the diffusion regime. A measure of the phase destroying scattering events is called the phase coherence length beyond which the phase of the waves is randomized. Not all scattering processes, however, destroy the phase. Elastic scattering processes such as scattering of phonons by impurities do not destroy phase. Thus, the phase coherence length is usually longer than the mean free path. The difference between mean free path and phase coherence length is typically small, however, particularly at room temperatures where inelastic scattering dominates, and we can treat the mean free path and the phase coherence length as the same.

The phonon wavelength in a crystal spans a wide range. Long wavelength phonons have a wavelength that is comparable to the crystal size. The shortest phonon wavelength is twice the lattice constant. However, not all the phonons in the wide range of wavelengths contribute equally to thermal transport. The actual probability of excitation for a specific phonon state depends on the energy of the state and the temperature of the object. We can estimate the order of magnitude of the average phonon wavelength, λ_t, by assuming that the average energy of one quantum state is $\kappa_B T/2$ and calculating the corresponding wavelength from the Planck relation $E=h\nu$ for phonons and photons. Here κ_B (=1.38x10^{-23} J/K) is the Boltzmann constant , h (=6.6x10^{-34} J·s) is the Planck constant and ν the frequency. This leads to,

$$\lambda_t = \frac{2hv}{\kappa_B T} \qquad (2)$$

where v is the speed of sound, λ_t is roughly equal to the thermal de Broglie wavelength and will simply be called the thermal wavelength. At room temperature, λ_t is ~10 Å in Si.

2.2 Wave vs. particle size effects

A key question in understanding phonon transport is whether one should treat phonons as waves or as particles. When treating them as waves, the phase information carried by waves should be included. The superposition of waves leads to interference, diffraction, and tunneling phenomena that also exist in other types of waves. Using the three characteristic lengths discussed above, we make the following qualitative observations.

One necessary condition for the inclusion of wave effects is that the mean free path should be comparable or longer than the structure characteristic length, such as the thickness of a film or the diameter of a wire. This condition, however, is not sufficient for actually observing the wave effects because of three additional factors: (1) the interface scattering processes, (2) the wavelength of the carriers, and (3) the spectrum of the carriers, as is explained below.[5]

When a wave meets an interface, it will be scattered. The most familiar example is the reflection and refraction of optical waves [7]. Phonon waves have similar processes. For a flat interface, the phases and directions of the refracted and reflected waves are fixed relative to the incident waves. Thus, these processes do not destroy phase. Periodic interface corrugations are another example for which the incident and outgoing waves have clear fixed phase relations. Rough interfaces, however, are more complicated. If the detailed interface roughness structures are known and if the interface interaction is elastic, the directions of the reflected and refracted waves can be determined in principle. In reality, this is rarely possible and rough interface scattering is often assumed to be diffusive, i.e., the reflected and transmitted waves are isotropically distributed into all

directions. Usually, the accompanying assumption is that the relationship between the phases of the reflected, transmitted and incident wave is lost, i.e., the scattering is phase randomizing. Such an assumption cannot be justified easily but appears to be true in many transport processes, particularly for phonons. In addition to elastic scattering, the inelastic scattering can be also strong at the interfaces and such scattering processes are phase breaking. Thus, the interface scattering can be approximated as phase breaking if the interface is rough, and as phase preserving if it is smooth. Whether an interface is rough or smooth depends on the average roughness, δ, compared to the wavelength λ. We can approximately take [5]

$$\frac{\delta}{\lambda} \begin{cases} \gg 0.1 & \text{(Rough)} \\ \ll 0.1 & \text{(Smooth)} \end{cases} \tag{3}$$

Thus, if interface scattering is diffuse, the wave aspects of energy carriers can be neglected and size effects, which appear when the characteristic dimension of the structure is comparable or larger than the mean free path, fall into the classical regime. The short phonon thermal wavelength suggests that the particle picture and classical size effects dominate except at very low temperatures when both mean free path and thermal wavelength are long. If the interface scattering processes preserve the phase relations, coherent waves may be established over the transport domain. Even under such situations, however, wave effects may still be unobservable because the spread in the phonon energy (wavelengths) may smear out any wave effects. The best analogous example is Young's interference experiments with light passing through two slits. The interference fringe is more easily observable for coherent incident light (as from a laser) than for incoherent white light.

3.   HEAT CONDUCTION IN NANOSTRUCTURES

In this section, we examine several heat conduction phenomena that are important at the nanoscale, including heat conduction at a single interface, and heat conduction inside thin films, nanowires and nanotubes.

3.1 Thermal boundary resistance

For heat conduction perpendicular to an interface, phonon reflection implies that energy transfer by heat carriers will be reduced compared to the case when there is no interface, or, equivalently, a resistance for heat flow exists at the interface. This phenomenon, called Kapitza resistance or thermal boundary resistance, has been known since the pioneering work of Kapitza for liquid helium-solid interfaces [8]. Extensive experimental and theoretical studies have been carried out in the past. At extremely low temperature when the phonon thermal wavelength is long, the interface reflection is close to specular,, models based on acoustic reflection and refraction for thermal boundary resistance agree well with experimental data. At room temperature, however, the phonon wavelength is short and diffuse scattering can be dominant. There is no proven easy way to model the phonon reflectivity and transmissivity for such diffuse scattering processes. For two solids in perfect contact, the thermal boundary resistance is on the order of 10^{-8}-10^{-9} m^{2}K/W. Such a thermal boundary resistance corresponds to the thermal resistance of a solid layer of thickness 1 nm - 1 μm with a bulk thermal conductivity of 1-100 W/m-K. When dealing with films of comparable thickness or smaller, the interface thermal resistance contributes significantly to the total thermal resistance.

3.2 Heat conduction in thin films, superlattices, nanowires, and nanotubes

A thin film has two interfaces. If the mean free path is longer than the film thickness, phonons will be scattered more frequently at the interfaces and may experience multiple scattering events. For heat conduction perpendicular to the film plane (cross-plane), the phonon reflection and the corresponding thermal boundary resistance phenomena add additional resistance to the heat flow, which is

manifested as a smaller effective thermal conductivity. Along the film-plane direction (in-plane), the thermal conductivity will be reduced if the interface scattering is diffuse, because diffuse scattering means some phonons that originally travel along the film plane direction are redirected backward. However, if the interface is specular, the classical size effect model leads to an in-plane thermal conductivity of a free-standing film identical to that of the bulk material. This is because the thin film acts simply as a waveguide for the heat flow. When the film thickness is thinner than the thermal wavelength, wave effects may be important. However, lattice dynamics calculations show that wave effects on the energy density and group velocity lead only to a small reduction in thermal conductivity for specular interfaces [9], although there are also suggestions that the scattering mechanisms will be significantly changed, which leads to a lower thermal conductivity. Quite extensive experimental studies have been carried out on the thermal conductivity of thin films, and Refs. [1, 2, 10] are good sources on the past work which should be consulted for more details.

Superlattices are periodic thin-film structures. Thermal properties of such structures have been studied over the last 15 years because of their importance for photonic and thermoelectric devices. Experimentally, it has been observed that superlattices have much lower thermal conductivities compared to the bulk values calculated based on the Fourier law, using the properties of their parent materials [10,11]. One potential explanation is the phonon spectrum change. Comparison with experimental data, however, shows that group velocity reduction alone can explain neither the magnitude of the cross-plane thermal conductivity reduction nor the reduction in in-plane thermal conductivity. The reason is that the lattice dynamics model assumes phase coherence of the phonons over the whole superlattice structure and does not include the possibility of diffuse interface scattering. Models considering classical size effects lead to reasonably good agreement with experimental data. These theoretical and experimental studies show that it is difficult to take advantage of the wave effects of phonons in heat conduction, primarily due to the short phonon thermal wavelength.

Thermal conductivity of nanowires is also attracting great interest. Naturally, the interest is in transport along the wire axis direction. If the surface of the wire is specular and there is no scattering inside the wire, energy transport is ballistic and phonon energy states are quantized. A universal phonon thermal conductance was predicted [12], and experimentally demonstrated at very low temperature under 0.8 K [13]. At slightly higher temperature (>3K), the diffuse interface scattering effects begin to appear. Experimental data on single nanowires at near room temperature are just becoming available on some nanowires and indicate a significantly lower thermal conductivity, again suggesting the importance of diffuse interface scattering [13,14]. In contrast to nanowires, a free-standing single wall carbon nanotube has all the atoms on the surface and the phonons can only propagate along the axial direction [15]. This latter attribute also means that unlike a solid nanowire in which the phonon modes inside the wire can hit the boundary (assuming boundary scattering is strongly phase breaking), phonons on the carbon nanotubes sheet have no boundaries to interact with. In addition, the strong modification of the phonon dispersion can also change the scattering mechanisms. It is thus suggested that carbon nanotubes can have a thermal conductivity even higher than that of diamond. Measurements and simulation data so far vary widely. Measurements on an isolated multiwall carbon nanotubes lead to high thermal conductivity values [16], but tangled and aligned carbon nanotubes have values orders of magnitude smaller [17]. At this stage, reasons for such a large discrepancy are unclear. It is quite possible that although a free-standing nanotubes has high thermal conductivities, a nanotube embedded in a host sees increased interface scattering which reduces its thermal conductivity values.

3.3 Nonlocal and ultrafast heat conduction

Size effects discussed in Sec. 3.1 and 3.2 are created due to the existence of interfaces. There are other situations where the Fourier law fails. These happen when the temperature gradient varies significantly within one mean free path. One example is MOSFET devices in which heat is generated

in a region of the order of 10 nmx10 nmx1 μm of the drain [18,[19]]. This heat source is much smaller than the phonon mean free path in the silicon substrate. In this case, the phonon temperature is much higher than the prediction based on the Fourier law. Another example is fast laser heating of a solid. The Fourier law leads to a diffusion length, $d \sim \sqrt{\Lambda vt / 3}$. If the diffusion length is comparable or smaller than the mean free path, heat conduction is no longer a diffusion process. Thus, we expect that the Fourier law fails for transient heat conduction processes occurring within,

$$t \ll 3\Lambda / v \leq 3\tau \tag{4}$$

Taking phonon mean free path in silicon as ~300 nm and an average phonon group velocity ~1000 m/s, the above criterion suggests that the Fourier law cannot be applied to heat conduction in silicon for processes shorter than 1 ns. Some photothermal diagnosis techniques routinely probe transient heat conduction processes much shorter than this time scale. For these applications, data analysis should be based on the Boltzmann equation rather than the Fourier law [4,5].

4.   APPLICATION TO THERMAL-ELECTRIC ENERGY CONVERSION

The nanoscale heat transfer phenomena discussed above have important implications for microelectronics, optoelectronics, data storage technologies, and energy conversion technologies [5]. An example is thermoelectric cooling and power generation based on the Peltier effect and the Seebeck effect, respectively [20]. The efficiency of a thermoelectric device is determined by the thermoelectric figure-of-merit of the material ZT $=\sigma S^2 T/k$, where S is the Seebeck coefficient, σ is electrical conductivity, k is the thermal conductivity and T is the absolute temperature. Currently, the best commercially available thermoelectric materials based on Bi_2Te_3 and its alloys have a ZT of around 1. Thermoelectric devices based on this material cannot compete in performance with other well-established technologies for energy conversion. Several approaches have been explored to increase the thermoelectric figure-of-merit. Among those, low-dimensional thermoelectric materials structures such as quantum wells, superlattices and nanowires have been extensively investigated [21]. Experimental results reported in past few years show that thermal conductivity reduction in nanostructures is a promising way to increase ZT [23,24].

5.   SUMMARY

This paper discusses some nanoscale heat conduction phenomena. Size effects occur when the heat heat carrier characteristic lengths, particularly the mean free path, become comparable or longer than the characteristic lengths of the structures or the transport processes (such as the diffusion length). A well-documented example is the reduced thermal conductivity in nanostructures such as thin films and superlattices, which has important implications for microelectronics, photonics, and thermoelectric energy conversion. The nanoscale heat transfer processes also have implications for fast laser materials interactions and photothermal diagnosis techniques that remain to be explored further.

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