

Thermal conductivity of dielectric nanowires with different cross-section shapes*

Gu Xiao-Kun(顾晓坤) and Cao Bing-Yang(曹炳阳)[†]

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education,
Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China

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Non-equilibrium molecular dynamics simulations have been performed to investigate the effect of the cross-section shape on the thermal conductivity of argon nanowires. Some typical cross-section shapes, such as triangle, square, pentagon, hexagon and circle, are carefully explored. The simulation results show that with the same cross-sectional area of the regular polygons, the thermal conductivities decrease with the reduction of the sides of the polygons, and the thermal conductivity of the circular nanowire is larger than those of the other polygonal ones. Phonon gas kinetic theory is used to analyse the phonon transport in nanowires, and the concept of equivalent diameter is proposed to illustrate the characteristic dimension of the none-circular cross-section.

Keywords: thermal conductivity, nanowire, phonon kinetic theory, molecular dynamics

PACC: 6670, 6865, 6322, 7115Q

1. Introduction

Recent years have witnessed the fast developments on the nanoscience and nanotechnology, such as microelectronics, optoelectronics, micro-/nano-electro-mechanical systems and biochip technology. It has been feasible to fabricate nanoscale devices,^[1–3] which provide one of the most efficient means to control electrical, optical, magnetic and thermoelectric properties of a functional material. Nanowire, as one of the basic building blocks for functional nanodevices, plays a crucial role in determining the performance of the nanoscale devices. Among a wealth of peculiar and fascinating properties, considerable attention has been paid to the heat transfer mechanisms and characteristics of a nanowire, and it is true that the stability and reliability of the nanoscale devices' performance are highly sensitive to the thermal property, for which a comprehensive analysis of thermal conductivities of nanowires is essential to both thermal design and thermal management in nanotechnology.^[4,5]

Albeit the results of experimental measurements of nanowires' thermal conductivity are convictive, the experiments not only suffer from testing apparatus, but also have difficulties in measurement techniques. To the authors' knowledge, the measurement of ther-

mal conductivity has only been made in size range of about 100 nm, while the nanowires ~20nm in diameter and hundreds of micrometres in length could be easily grown.^[6,7] So, theoretical and numerical approaches, including molecular dynamics (MD),^[8,9] Monte Carlo (MC) simulation^[10] and variations of the Boltzmann transport equation (BTE),^[11] are proposed to gain the thermal conductivity of the nanostructures. The method of MD simulation, as a powerful tool to study the nanoscale thermal transport, especially, could give microscopic interpretations of phenomena which are either hard to illustrate in theory or difficult to be observed in experiment at atomic scale.

Studies^[9–13] up to now have revealed that the thermal conductivity of nanowires could be much smaller than bulk value, and exhibit a significant size effect. The size dependence of the thermal conductivity is basically a result of heat carrier scattering at boundaries, as the dimension of a one-dimensional nanostructure is reduced to the range of mean free paths (MFPs) of heat carriers.^[14,15] This unique characteristic is desirable in such applications as thermoelectric cooling and power generation, while it is not preferable for electronics, photonics etc.

Many research groups have succeeded in synthesizing nanowires with different cross-sections using

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[†]Corresponding author. E-mail: caoby@tsinghua.edu.cn

different methods, most of which are potential approaches to mass production. Bae *et al*^[16] synthesized triangular cross-section nanorods with an average diameter of 50nm by chemical vapour deposition using the reaction of gallium/gallium nitride with ammonia. Pan *et al*^[17] synthesized nanobelts, which have a rectangle-like cross-section with typical widths of 30 to 300 nm, width-to-thickness ratios of 5 to 10 by simply evaporating the desired commercial metal oxide powders at high temperatures. Agarwal *et al*^[18] reported that silicon nanowires were fabricated on bulk silicon and silicon on insular (SOI) wafers by means of conventional Si process technology, and the cross-section of the nanowires is typically triangular, which can then be converted to circular using high temperature annealing. However, the cross-section dependence of the thermal conductivity is seldom reported previously.

This paper focuses on the thermal conductivity of dielectric nanowires with different shapes of cross-sections. Heat conduction through argon crystal nanowires is investigated by the method of non-equilibrium molecular dynamics (NEMD) simulations. Theoretical analyses, based on phonon gas kinetic theory, are also performed to interpret the simulation results, which shows that introduction of equivalent diameter is capable to characterize the thermal con-

ductivity of nanowires of non-circular cross-sections.

2. Molecular dynamics simulation

The NEMD simulations use argon crystal as the model system for its reliable experimental data and its widely accepted potential function of atom interactions. The atom interaction in solid argon can be accurately described by the Lennard-Jones potential:

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r is the atom separation, ε is the energy parameter and σ is the diameter parameter. The units of the physical parameters used in our simulations are given in Table 1. An argon face-centred-cubic (FCC) crystal is placed at the centre of the calculation domain, and the origin of the coordinates is set at the centre as well. Periodic boundary conditions are imposed along x -axis. Though the argon nanowires may not exist in reality, it is reasonable and efficient to obtain the simulation results for the accurate potential in the form of Lennard-Jones. The law based on the thermal conductivity of argon nanowires can be extended to other dielectric materials.

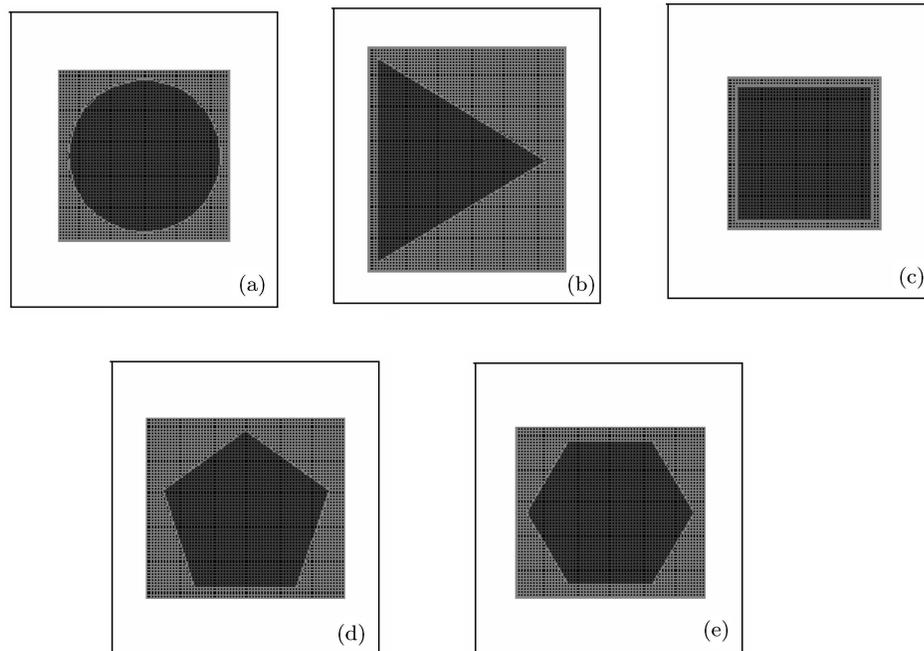


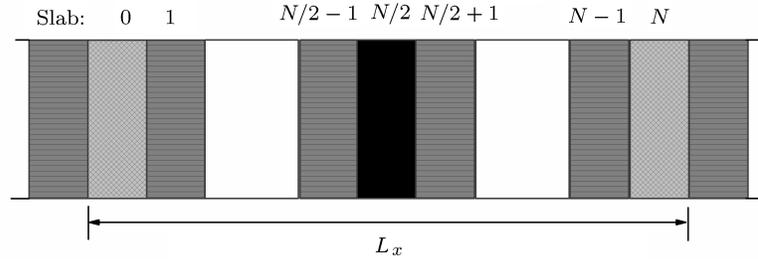
Fig.1. Cross-sections of nanowires: circular (a), triangular (b), square (c), pentagonal (d) and hexagonal (e).

Table 1. Units of the physical parameters.

Energy	Length	Mass	Temperature	Time
$\varepsilon/10^{-21}$ J	$\sigma/10^{-10}$ m	$m/10^{-26}$ kg	$(\varepsilon/k_B)/K$	$\tau_0 = \sigma(m/\varepsilon)^{1/2}/10^{-12}$ s
1.67	3.405	6.64	119.8	2.16

Reported in this article are thermal conductivities of nanowires with various shapes of cross-section but with a consistent cross-section area of $547.2\sigma^2$, and 22000–44000 atoms are simulated depending on the shapes and areas of cross-sections. Bulk crystal and nanowires with triangular, square, pentagonal, hexag-

onal and circular cross-sections are modelled as shown in Fig.1. Fixed boundary conditions on the outer surface of the nanowire are introduced to avoid evaporation from the nanowire domain during the simulation process.

**Fig.2.** The reverse scheme for NEMD simulations of heat conduction in nanowires.

A reverse scheme for the NEMD method^[19] is used to calculate the thermal conductivities of the nanowires. In this method ‘cold’ and ‘hot’ regions are defined as shown in Fig.2, and the heat flux is created by exchanging the velocity of the hottest atom in the cold region with that of the coldest one in the hot region. After reaching steady state, the energy imposed by the exchange of the velocity between the hot and cold slabs is exactly balanced by heat conduction. Then the energy transported by velocity exchange is summed up, the resulting temperature profile is also measured at the same time. The thermal conductivity is calculated from the known heat flux due to the velocity switching, the temperature gradient at equilibrium between the two regions, and the cross-sectional area of the nanowire:

$$\lambda = -\frac{\sum \frac{m}{2}(v_h^2 - v_c^2)}{2tS\langle \partial T / \partial x \rangle}, \quad (2)$$

where $\langle \rangle$ donates the statistical average over the simulation time, the subscripts h and c refer to the hot and the cold atoms whose velocities are interchanged, and S and t are the cross-sectional area and the simulation time, respectively. All the above properties of the reverse scheme guarantee the conservation of the total momentum and energy automatically.

In calculation, in order to optimize the computa-

tion of the atom interactions, a linked-list data structure is adopted and a hybrid method of cell subdivision and neighbour list is introduced. Hamilton’s classical equations of motion are numerically integrated with a Leapfrog Verlet algorithm^[20] with a fixed time step of about 10 fs, which is far smaller than the phonon relaxation time (of the order 1.0 ps). Besides, the cutoff distance is set at 2.5σ .

3. Simulation results and discussion

In the simulations of nanowires with different cross-sections, the mean temperature of the systems is kept at 40K, and the maximum temperature difference between the ‘cold’ and ‘hot’ regions is 3 K. Figure 3 shows the temperature profiles for the five nanowires with different cross-sections at 40K along the longitudinal direction. Firstly, it is noted that the temperature profiles are nearly linear in the middle region away from the cold and hot slabs, indicating that Fourier’s heat conduction law is still valid, and as a result it is reasonable to use Eq.(2) to calculate the thermal conductivity of the nanowires. Secondly, the simulation domain is divided into two similar regions, which are of good symmetry and, especially, in almost

the same temperature distribution. In fact, each of the regions can be used to calculate the temperature gradient, but considering the time-consuming computation of the temperature profile, averaging these two intermediate temperature profiles may be an efficient method to reduce the local temperature fluctuation and improve the temperature profiles as well. Thirdly, the temperature gradients near the cold and hot regions are much larger than the rest of the nanowire, the reason of which is the local nonequilibrium phenomenon near the heated slabs. In addition, though the difference between the curves in Fig.3 seems not very evident, the thermal conductivities depending on both the slope of the curve and the heat flux may differ greatly as depicted below.

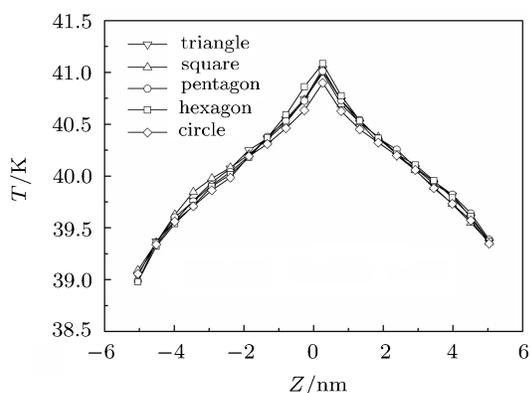


Fig.3. Temperature profiles of five nanowires with different shapes of cross-sections at 40 K.

In Fig.4, the results from molecular dynamics simulation are plotted for observing the cross-section shape effect on the thermal conductivity of the nanowires (the theoretical data will be discussed in detail below). The number of sides of the polygons is changed to construct nanowires of different cross-sections from three to six, as well as the circular section. Compared with the MD results of the thermal conductivity of bulk solid argon at $T = 40$ K, 0.56 W/mK,^[21] the thermal conductivities of the five nanowires with different cross-sections are about 50%–70% of the bulk solid argon. A remarkable size effect can be observed on the thermal conductivity of the nanowires. Moreover, under the simulation condition, as the side of the shape of nanowires' cross section increases, the thermal conductivity increases. In addition, the nanowire with circular cross-section has the largest thermal conductivity among the nanowires with the same cross-sectional area. So it is not negligible to consider the effect of the shape of the cross-

sections when calculating the thermal conductivities of different nanowires.

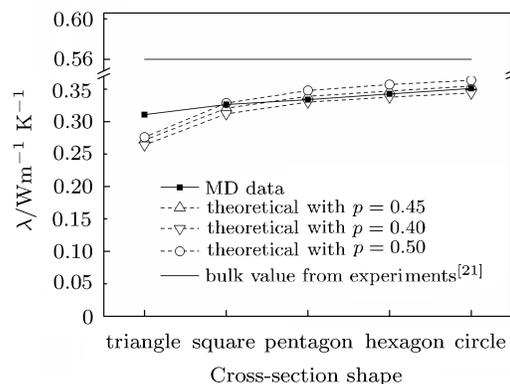


Fig.4. Thermal conductivities of nanowires versus the shape of cross-section. The solid squares linked by a solid line are from the MD simulations and open symbols linked by dashed lines are results based on phonon gas kinetic theory.

Because heat conduction in a dielectric solid depends mainly on the lattice vibration in the nano-scale structures, the lattice vibration and thus the heat conduction are greatly influenced by the nanowires' surfaces. The surfaces are the interfaces of the nanowires and rigid boundaries in the present simulations, the surface's configuration is remarkably different from the bulk configuration, and the atomic bond disconnects so that the mean free path of phonons is remarkably decreased. The influence of phonon boundary scattering gradually increases, resulting in the decrease of thermal conductivity with increasing ratio of surface area to volume.

According to the phonon gas kinetic theory,^[22] regarding the heat carriers in the solid argon as gas molecules, the lattice thermal conductivity can be written as

$$\lambda = \frac{1}{3} C_v v \Lambda, \quad (3)$$

where C_v is the heat capacity per volume, v is the sound velocity, and Λ is the phonon MFP. As for the nanowires with different cross sections, the MFPs are obviously different. Taking into account the complexity of calculating the of MFPs the non-circular cross-section nanowires, Eq.(4)^[23] is employed to estimate the MFPs under different conditions.

$$\zeta_i = \frac{A_{NW_i}}{A_{Bulk}} = 1 - \frac{1 - (1 - p) \cdot \exp(-|\mathbf{r} - \mathbf{r}_B|/\Lambda_{Bulk})}{1 - p \cdot \exp(-|\mathbf{r}_B - \mathbf{r}_{B'}|/\Lambda_{Bulk})}, \quad (4)$$

where p is the parameter characterizing the interface roughness and its effect on the phonon-boundary scat-

tering; Λ_{Bulk} , Λ_{NW} is the average phonon MFPs of the bulk and nanowires. This ratio represents the correction implied by the size effect. r , r_B and $r_{B'}$ are the position where the specularly reflected beam previously left the surface (as shown in Fig.5).

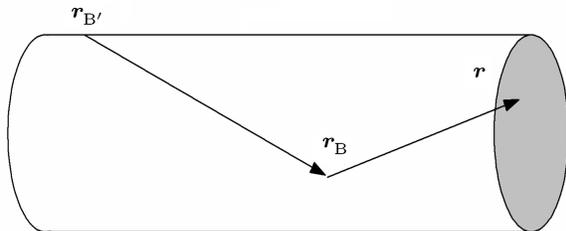


Fig.5. Model of phonon transport in nanowires.

Numerical results of Eq.(4) are plotted as lines in Fig.4. This implies that MD data are in good agreement with the calculation of MFPs when the interface specularity parameter p is about 0.45. Obviously, there exists a significant size effect on the thermal conductivity in nanowires. The influence of the difference between boundary scatterings of nanowires with different cross-sections, to some extent, contributes to the decrease of the thermal conductivity with the reduction of the sides of the polygons, or with the reduction of the perimeter of the cross section.

Considering the simplicity of the geometry of the circular nanowires, lots of simple but effective models dealing with circular ones have been proposed, showing their strong ability in calculating the thermal conductivity.^[11,19] In engineering, non-circular nanowires are easy to obtain, especially the trapezoid cross-section nanowires. To overcome the difficulty of theoretical models, we define the hydraulic diameter as the equivalent diameter in place of the characteristic diameter of non-circular-cross-section nanowires, as does in fluid mechanics,^[24]

$$D_h = \frac{4S}{P}, \quad (5)$$

where S is the cross-sectional area of the nanowire, P is the perimeter of the cross section. D_h makes it possible to unitize the proposed models that deal with cylindrical nanowires.

The thermal conductivities of nanowires with non-circular cross-sections can be calculated according to the above equations. Figure 6 shows a comparison between the results of equivalent-diameter model and those of the MD simulation.

As shown in Fig.6, the results of the phonon gas kinetic theory are in an acceptable agreement with the MD simulation data, showing that the decrease of hydraulic diameter will lead to the reduction of the boundary scattering relaxation time and thus reduces the thermal conductivity as the sides of the shape of the nanowires' cross section reduce. We can see that equivalent diameter offers a powerful tool to the thermal conductivity calculation for non-circular nanowires.

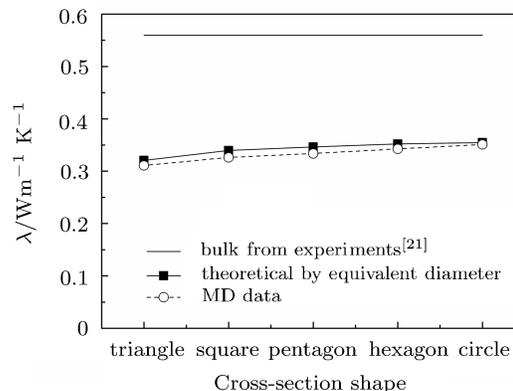


Fig.6. Thermal conductivities obtained by MD simulation and the gas kinetic theory with equivalent diameter as the characteristic diameter.

4. Conclusions

We have presented NEMD simulations for calculating the thermal conductivities of solid argon nanowires with different shapes of cross-sections. The regular triangle, square, pentagon and hexagon are used in the calculations. The simulation results show that with the same cross-sectional area in the regular polygons, the thermal conductivity decreases with the reduction of the number of sides of the polygons, and that the conductivity of circular nanowires is the largest among the polygons. The MD results reveal a significant size effect on the shape of nanowire cross sections. Theoretical analyses based on phonon gas kinetic model are also carried out, and the theoretical results are in good agreement with the MD data when the sides of polygon are larger than four, with an interface specularity parameter of 0.45. The concept of equivalent diameter approximation is proposed to be used as the characteristic dimension of the non-circular cross-section, and our MD data verify the reasonability of this kind of approximation.

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