Thermal conductivity of graphene mediated by strain and size

CrossMark

Youdi Kuang [a,b,c], Lucas Lindsay [d], Sanqiang Shi [c,e,*], Xinjiang Wang [a], Baoling Huang [b,*]

[a] College of Science and Engineering, Jinan University, Guanzhou, China
[b] Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
[c] Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
[d] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[e] Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen, China

ARTICLE INFO

ABSTRACT

Based on first-principles calculations and full iterative solution of the linearized Boltzmann–Peierls transport equation for phonons, we systematically investigate effects of strain, size and temperature on the thermal conductivity k of suspended graphene. The calculated size-dependent and temperature-dependent k for finite samples agree well with experimental data. The results show that, contrast to the convergent room-temperature $k = 5450$ W/m-K of unstrained graphene at a sample size $\sim$8 cm, k of strained graphene diverges with increasing the sample size even at high temperature. Out-of-plane acoustic phonons are responsible for the significant size effect in unstrained and strained graphene due to their ultralong mean free path and acoustic phonons with wavelength smaller than 10 nm contribute 80% to the intrinsic room temperature k of unstrained graphene. Tensile strain hardens the flexural modes and increases their lifetimes, causing interesting dependence of k on sample size and strain due to the competition between boundary scattering and intrinsic phonon–phonon scattering. k of graphene can be tuned within a large range by strain for the size larger than 500 μm. These findings shed light on the nature of thermal transport in two-dimensional materials and may guide predicting and engineering k of graphene by varying strain and size.

1. Introduction

Graphene, a two-dimensional (2D) sheet of carbon atoms, has attracted great interest in recent years due to its extraordinary mechanical, chemical, electronic and thermal properties. The experimentally reported ultrahigh thermal conductivity k (up to 5300 W/m-K) [1] of graphene renders it the most thermally conductive material, and of promise for thermal management applications [2–4]. Moreover, graphene provides a benchmark model for the study of thermal transport in 2D materials. Therefore, intensive efforts have been committed to understand the underlying thermal transport physics in graphene experimentally [1,5–16] and theoretically [2,17–30].

Previous experimental studies [1,5,6,10] using an opto-thermal Raman technique have reported k values of suspended graphene that scatter significantly, ranging from 600 [10] to 5300 [31]

W/m-K even with temperature effects accounted for. Using direct thermal-bridge measurements, Xu et al. [7] recently observed significant size effects on k of graphene and reported that k diverges logarithmically with sample length; in contrast, previous Raman experiments did not discern a size-dependence of k [1,6]. Pettes et al. [11] found that k of graphene may be significantly influenced by the residual polymeric layer produced during the transfer process of graphene. It can be seen from previous experiments that measured k depends strongly on various extrinsic factors including sample size, process conditions, sample quality, measurement method and substrate coupling [12,13], all giving large scatter in experimental k data.

On the theoretical side, fundamental problems concerning the details of thermal transport in graphene have been subjects of debate [17–30], including the convergence behavior of k with system size, the extent of the diffusive and ballistic transport regimes, the role of flexural acoustic (ZA) phonons for thermal transport and strain effects on the convergence of k. It is generally believed that acoustic phonons [31] dominate the thermal transport in graphene. Based on this, 2D models give a logarithmic divergence with system size [27] but neglect the contributions from ZA phonons due to their low group velocities near the center of first

* Corresponding authors at: Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong. Tel.: +852 27667821 (S. Shi). Tel.: +852 23587181. (B. Huang).
E-mail addresses: san.qiang.shi@polyu.edu.hk (S. Shi), mebhuang@ust.hk (B. Huang).

Brillouin zone (FBZ) and their large Grüneisen parameters [32]. However, molecular dynamics (MD) simulations [17,18,26,29,30] with large system sizes have reported that room-temperature k of graphene converges, though at values much lower than experimental results on finite-size systems.

First-principles lattice dynamics calculations [22,24,28] of k of graphene within three-phonon scattering framework have also been conducted. Using the single-mode relaxation time approximation (SMRTA), Bonini et al. [22] showed that k of infinite graphene diverges under infinitesimal isotropic tensile strains, while k converges to ~550 W/m-K for infinite unstrained graphene at room temperature. The results are partly different with aforementioned MD predictions [18] that k of infinite graphene diverges only under large tensile strain (>0.02). We note that the SMRTA incorrectly treats the momentum-conserving Normal (N) processes as independent resistive processes on the same footing as Umklapp (U) processes [33], and it cannot be used to appropriately present the phonon thermal transport in graphene, as justified by Lindsay et al. [23] and Fugallo et al. [28]. Based on a full iterative solution of the linearized Boltzmann–Peierls Equation (BPE), Lindsay et al. [23] found that ZA phonons give the dominant contributions to k in finite graphene up to 50 μm with strong dependence of k on boundary scattering; Fugallo et al. [28] found that room temperature k of unstrained graphene with a size of 1000 μm is up to 4300 W/m-K, close to the reported highest experimental value [31]. Although the previous works provided excellent insights into understanding thermal transport of graphene, many conclusions apply to finite graphene because of the compulsively adopted boundary constraint. It can be seen clearly from the literature that the following fundamental problems still remain unclear: (1) k convergence in strained graphene by full solutions of BPE; (2) the role of ZA modes in k of strained graphene at different temperatures; (3) the scattering behavior of low-frequency phonons at the long-wavelength limit; (4) the interplay of strain and size effects.

In this work, we intend to elucidate these problems using a rigorous first principles BPE for phonon transport approach with and without applying boundary constraint. Full iterative solutions of the linearized BPE from reciprocal-space calculations and further mathematical analysis show that with increasing system size k converges for unstrained graphene and diverges for strained graphene. Mode contribution analysis shows that ZA phonons are the major heat carriers and control the convergence behaviors in both unstrained and strained graphene up to 3000 K. Further, the long mean free paths of ZA phonons make finite size effects on k persistent up to ~8 cm for unstrained graphene. The joint effect of strain and size on k of finite graphene is also clarified, which makes it promising to tune k of graphene in a large range when the sample size is larger than 500 μm. Considering the large graphene fracture strain (~0.25) and recently successfully fabrication [34] of single crystal graphene sample with the size of a few centimeters, mediating k of graphene by tensile strain and size is of practical significance.

2. Computational methodologies

A microscopic description of the lattice thermal conductivity k can be derived from BPE for phonons [21,22,24,35] within the three-phonon scattering framework. Considering the isotropic thermal conductivity of infinite graphene, along an in-plane crystallographic direction α, the intrinsic k is calculated by the following equation [23,35]:

$$k = k^{\alpha\alpha} = \sum_{\lambda} k_{\lambda} = \frac{1}{k_B T^2 V N_1^2} \sum_{\lambda} f_{\lambda}(f_{\lambda} + 1)(\hbar\omega_{\lambda})^2 v_{\lambda}^{\alpha} v_{\lambda}^{\alpha} \tau_{\lambda}, \quad (1)$$
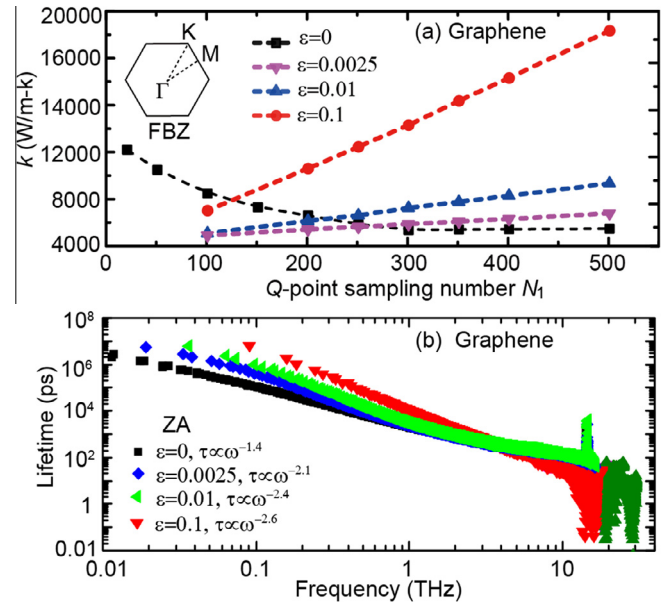

Fig. 1. (a) Convergence of k of graphene with q-point sampling density for different isotropic tensile strains. (b) Lifetimes of ZA phonons in graphene under different strains.

where λ represents a phonon mode with wavevector $\mathbf{q}$ and branch index j. k_{λ} is the contribution of mode λ to k. ω_{λ}, v_{λ}^{α}, and τ_{λ} are the angular frequency, group velocity and phonon lifetime, respectively. k_B, $\hbar$, f_{λ} are the Boltzmann constant, the reduced Plank constant and the Bose–Einstein distribution of phonons at temperature T, respectively. V is the volume of the graphene unit cell with a thickness of 0.335 nm [23]. This work combines an iteratively self-consistent solution to the linearized BPE with harmonic and anharmonic interatomic force constants (IFCs) from Density Functional Perturbation Theory (DFPT) and Density Functional Theory (DFT) calculations [23,24], respectively, using the QUANTUM ESPRESSO package [36] within the local density approximation (LDA) and using a norm-conserving pseudopotential to represent the core carbon electrons. Before calculating IFCs, the 2-atom unit cell of unstrained graphene is optimized fully along three axial directions to minimize the internal stress. The convergence precisions for energy and atomic force are taken as 1×10^{-10} eV and 1×10^{-7} eV/Å, respectively, to ensure the absolute value of in-plane stress is less than 0.01 kbar. To determine the harmonic IFCs, DFPT calculations are employed with a 13×13 k-point mesh and 120 Ryd plane-wave cutoff for the 2-atom unit cell. To determine the interatomic forces and resulting anharmonic IFCs, DFT calculations with Γ-point sampling in slightly perturbed 162-atom supercells with a 100 Ryd plane-wave cutoff are used. For harmonic IFCs of unstrained graphene, the translational and rotational invariance conditions are enforced using the acoustic sum rules proposed in the work by Bonini et al. [22]. Only translational invariance conditions are applied to harmonic IFCs of strained graphene. For anharmonic IFCs, translational invariance is enforced via a χ^2 fitting procedure described in Ref. [37]. We note that the accuracy of these anharmonic IFCs was tested and discussed in Ref. [37]. Further technical details for the calculations of dispersion relations and three-phonon scattering rates can be found elsewhere [23,35]. In order to judge the convergence of intrinsic k at large grid density ($N_1 > 200$), a modified ShengBTE code [35] is used to calculate k iteratively based on these IFCs. Comparison of the calculated dispersion of graphene with experimental data [38,39] gives excellent agreements. The full 2D FBZ (Fig. 1a) is discretized into a Γ-centered regular $N_1 \times N_1$ grid with N_1 up to 501 considered in this study.