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Manuscript Draft

Manuscript Number: CPLETT-15-396R2

Title: Length, Width and Roughness Dependent Thermal Conductivity of Graphene Nanoribbons

Article Type: Regular Article

Section/Category: Nanostructures and Materials

Corresponding Author: Dr. Sanjeev Gupta, PhD

Corresponding Author's Institution: St. Xavier's College

First Author: Yogesh Sonavane, Ph.D.

Order of Authors: Yogesh Sonavane, Ph.D.; Sanjeev Gupta, PhD; Pooja Raval, M.Sc.; Igor Lukačević, Ph.D.; P. B Thakor, Ph.D.

Abstract: This letter reports on the investigation of temperature dependent thermal conductivity along a long free-standing graphene nanoribbon (GNR) by a one-dimensional direction-dependent phonon-boundary scattering in the frame of linearized phonon Boltzmann transport method. It is observed that GNR has highly length and width dependent thermal conductivity due to the difference between in-plane and out-of-plane phonon modes in the phonon dispersion curve. We show that phonon mediated thermal conduction increases with size, while it decreases with increasing edge roughness. These results are relevant for tailoring and engineering of the thermal conductivity of graphene nanoribbons in thermoelectronic and photonic devices.

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Dear Editor,

Thank you very much for your mail along with the referee's report on our paper and allowing us to submit our revised paper late. We have thoroughly revised our paper considering the comments of learned referees. Indeed, I am very much thankful to the learned referee for positive review of the paper and positive and useful comments, which helped us to clarify the presentation and discussion of the results reported in this paper. Based on their comments, we have revised our paper and resubmitting for your kind perusal. The detailed reply to the learned referee's comments is given below and I hope the present manuscript will find its way to the publication.

Sincerely yours,

Sanjeev Gupta

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Dear Reviewers,

We have revised our manuscript according to Your suggestions. Hopefully, You will find now our manuscript appropriate for publishing.

Sincerely yours,

Sanjeev Gupta

Answers to Reviewer #1:

We appreciate the referee for his/her valuable comments. These comments are useful to improve our paper.

1) The comparison of the author`s present work with the previous reports (ref. 1, 2, 3) must be a part of manuscript. Authors have explained the comparison in answer to reviewers (Point-3 reviewer-1).

   We have included the mentioned comparisons in the manuscript (Introduction, page 3, paragraph 2), just after references 1, 2 and 3 are introduced in paragraph 1.

2) English language in the text has been improved.

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Highlights

1. Thermal conductivity of graphene nanoribbons increases with nanoribbon length.
2. Thermal conductivity of graphene nanoribbons increases with nanoribbon width.
3. Thermal conductivity of graphene nanoribbons decreases with edge roughness.
4. Contribution of flexural phonons decreases with the size of lateral confinement.

*Graphical Abstract (pictogram) (for review)

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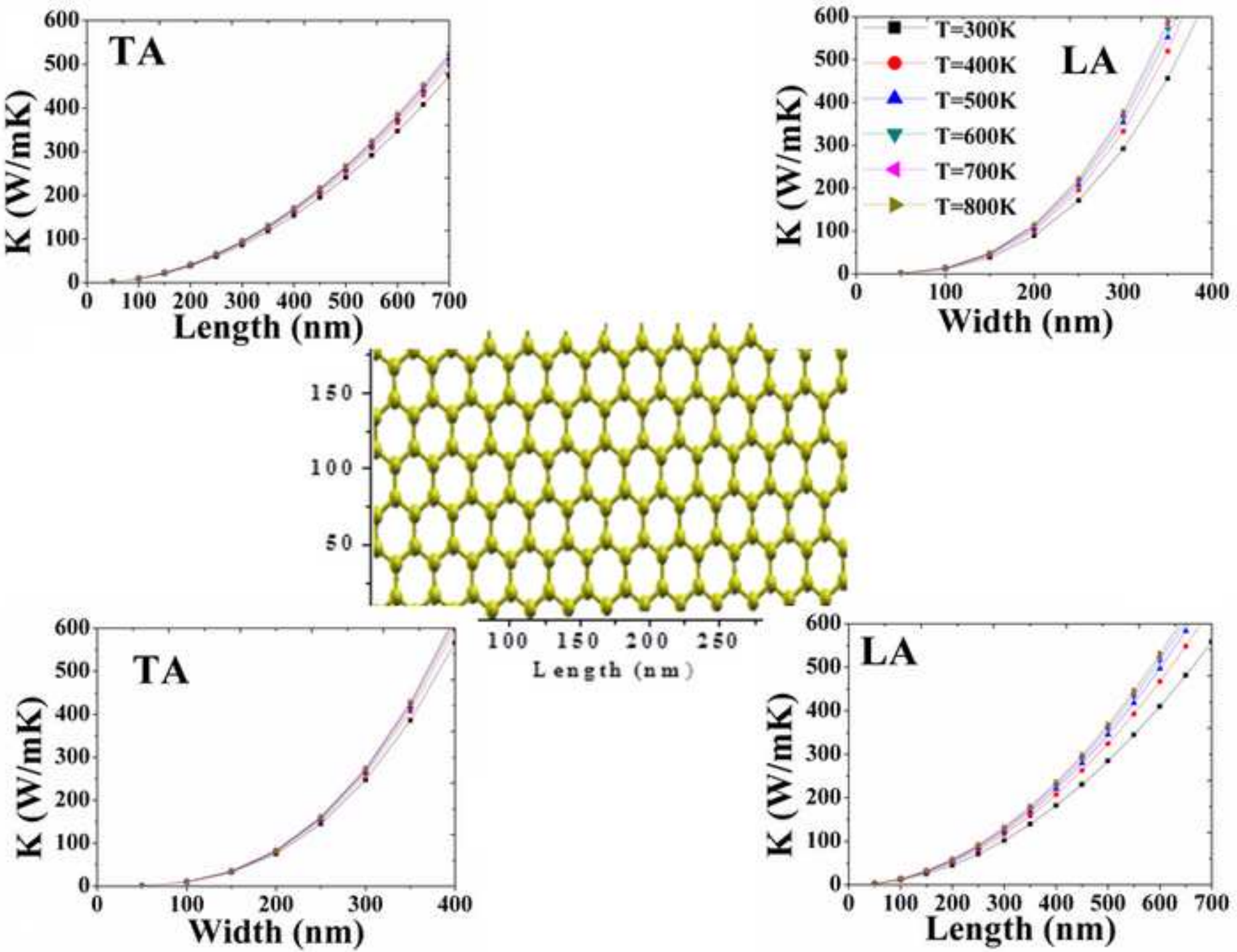

Length, Width and Roughness Dependent Thermal Conductivity of Graphene Nanoribbons

Yogesh Sonvane[1], Sanjeev K. Gupta[2,*], Pooja Raval[1], Igor Lukačević[3], and P. B. Thakor[4]

[1]Department of Applied Physics, S. V. National Institute of Technology, Surat, 395007, India

[2]Department of Physics, St. Xavier's College, Ahmedabad, 380009, India

[3]Department of Physics, University J. J. Strossmayer, Osijek, 31000, Croatia

[4]Department of Physics, Veer Narmad South Gujarat Univeristy, Surat, 395007, India

This letter reports on the investigation of temperature dependent thermal conductivity along a long free-standing graphene nanoribbon (GNR) by a one-dimensional direction-dependent phonon-boundary scattering in the frame of linearized phonon Boltzmann transport method. It is observed that GNR has highly length and width dependent thermal conductivity due to the difference between in-plane and out-of-plane phonon modes in the phonon dispersion curve. We show that phonon mediated thermal conduction increases with size, while it decreases with increasing edge roughness. These results are relevant for tailoring and engineering of the thermal conductivity of graphene nanoribbons in thermoelectronic and photonic devices.

Keywords: Graphene nanoribbon, Phonon, Thermal conductivity

[*]Corresponding author: Dr. Sanjeev K. Gupta (sanjeev.gupta@sxca.edu.in)

2D layered honeycomb network based on sp^2 bonded carbon structures, which is well known in literature as 'Graphene', is the smallest building unit of most carbon family materials. The unique properties like electronic, thermal, transport and mechanical properties have been given hope for improvement in future nanodevices. Graphene nanoribbons (GNR), where charge carriers are confined in two dimensions and free to move along the ribbon axis, have attracted much attention nowadays as they are realized by lithographic routes, by unzipping nanotubes, or by various chemical routes, like chemical vapour deposition. Recently, GNRs have emerged as a potential few-atom-thick material in width and length, which are considered as important parameters for tailoring the carbon based nanoelectronics. GNRs have, thus, emerged as important candidates for thermoelectric applications with high figure-of-merit, due to this external arrangement of atoms which affects its thermal transport. Furthermore, the precise knowledge of effect of width and edge roughness in GNRs can give rise to unusual physics. A large growing number of experimental and theoretical investigations [1-27] have been performed to study the thermal properties, specially thermal transport assisted by phonon vibrations.

Han and Kim have performed experiments [18], and carried out systematic studies of the scaling of transport gap in GNRs of various dimensions. They have found evidence of a transport mechanism in disordered GNRs based on hopping through localized states whose size is close to the GNR width.

Nika et al [1,2] performed a detailed study of the lattice thermal conductivity of graphene using the phonon dispersion obtained from the valence-force field (VFF) method. They have used three-phonon Umklapp scattering directly considering all phonon relaxation channels allowed by the energy and momentum conservation in graphene 2D Brillouin zone. They have studied thermal conductivity of graphene flake as a function of temperature for several different lengths of the flake. Their model obtained two Grüneisen parameters for the

longitudinal (λ_{LA}) and transverse (λ_{TA}) phonon branches through averaging over phonon modes, which were obtained from *ab initio* calculations. Jiang et al [3] calculated the thermal conductance of graphene in the pure ballistic limit obtaining a high value which translates to the thermal conductivity in excess of ~6600 W/mK. Ghosh et al. [4] have experimentally found that graphene suspended across trenches in Si/SiO_2 wafer has thermal conductivities in the range of 3000–5000 W/mK depending on the specific sizes, which vary from 1 to 5 µm.

Numerical and *ab initio* calculations have shown that there is a strong need for a simple analytical model, based on phonon Boltzmann transport equation in the relaxation time approximation, taking into account Umklapp phonon-phonon scattering and phonon-boundary scattering processes, and, most importantly, not confined on ballistic transport regime, which can explain the differences in the phonon transport in graphene nanoribbon, a spatially bounded layer of graphene, at different temperatures due to different edge types and lateral confinements: lengths and widths. Our hypotheses is that these parameters are crucial, through different phonon scattering mechanisms and availability of certain phonon modes, for understanding the behavior of thermal conductivity in GNR and are, thus, relevant for applications of GNRs in (thermo)electric and photonic devices. In addition, we have calculated thermal conductivities of phonon longitudinal acoustic (LA) and transverse acoustic (TA) branches, which carry heat [1,2,28,29]. Separate analysis of longitudinal and transversal branch contributions allows us to gain better understanding of phonon dispersions and its characteristics as the main activators of heat conduction in GNR.

Thermal conductivity of graphene nanoribbons have potential applications in nanoscale thermal management such as on-chip cooling and energy conversion by controlling the phonon heat transport which is also fundamental in several recently proposed novel schemes of “thermal circuits” or information processing [26]. Our investigation of the thermal conductivity and of controlling mechanisms by longitudinal acoustic (LA) and

transverse acoustic (TA) phonon branches in graphene nanoribbon can be important for the development of energy-efficient nanoelectronics based on graphene. Rapid development on the experimental side, provides an ample opportunity for theorists to test their models to understand the quantum phenomena which dictate phonon modulation in GNRs.

General expression for the thermal conductivity of graphene can be written as [1,2],

$$\kappa_\lambda = \frac{S}{(2\pi)^2}\int c_{ph}\ v_\lambda^2\ \tau_\lambda\ d\vec{q} = \frac{S}{(2\pi)^2}\int_0^{q_{max}}\int_0^{2\pi}\frac{k_B}{S\delta}\frac{\left[\frac{\hbar\omega_\lambda(q)}{k_BT}\right]^2\ exp\left(\frac{\hbar\omega_\lambda(q)}{k_BT}\right)}{\left[exp\left(\frac{\hbar\omega_\lambda(q)}{k_BT}\right)-1\right]^2}\upsilon_\lambda^2(q)cos^2\theta\ \tau_\lambda(q,\theta)qdqd\theta \quad (1)$$

where λ = *LA, TA*. *S, C_{ph}* , ħ , k_B , *T and q*, are the area of the sample, volumetric specific heat of each mode, reduced Planck constant, Boltzmann constant, absolute temperature and wave vector, respectively. Here $v_{\lambda,y}$ is the *y* component of the group-velocity vector in branch λ. δ = 0.35 *nm* is the effective layer thickness, θ (ranging from 0 to 2π) is the angle between the wave vector and *y* axis, and $q_{\max}$ is the cut-off wave vector and ω_λ [1,2,6] is given by

$$\omega_\lambda(q) = \nu_\lambda q \quad \lambda = LA, TA \quad (2)$$

In this work, we do not consider other scattering mechanisms such as defects. Therefore, according to the Matthiessen's rule, $\tau_\lambda^{-1}(q,\theta) = \tau_{U,\lambda}^{-1}(q) + \tau_{B,\lambda}^{-1}(q,\theta)$, where $\tau_{U,\lambda}(q)$ and $\tau_{B,\lambda}(q,\theta)$ are relaxation times of Umklapp phonon-phonon scattering and phonon-boundary scattering respectively. $\tau_{U,\lambda}(q)$ is given as [1,6]

$$\tau_{U,\lambda}(q) = \frac{M\upsilon_\lambda^2(q)\omega_{max,\lambda}}{\gamma_\lambda^2 k_B T\omega_\lambda^2(q)} \quad (3)$$

M, γ_λ and $\omega_{max,\lambda}$ are mass of a graphene unit cell, Grüneisen parameter and maximum cut-off frequency for each branch λ, respectively. It controls the strength of the phonon-phonon scattering process for each branch.

The proper treatment of phonon-boundary scattering rate is critical in nanoscale system, especially when the characteristic size of the system is close to or less than the phonon mean free path. $\tau_{B,\lambda}(q,\theta)$ is given as [7]

$$\tau_{B,\lambda}(q,\theta)=\begin{cases} l_l(\theta)/\upsilon_\lambda(q) & if\ \ l_l<l_e \\ l_e(\theta)/\upsilon_\lambda(q) & otherwise \end{cases} \tag{4}$$

where l_e is the averaged distance traveled ballistically by a phonon before hitting the end boundary, and l_l is the averaged distance traveled ballistically by a phonon before hitting the lateral boundary. l_l and l_e are given as follows,

$$l_e(\theta)=\frac{1}{L|cos\,\theta|}\int_0^L ydy=\frac{L}{2|cos\,\theta|} \tag{5}$$

$$l_l(\theta)=\frac{1}{W|sin\,\theta|}\int_0^W ydy=\frac{W}{2|sin\,\theta|} \tag{6}$$

where L and W are length and width of GNRs.

The parameters for dispersion originate from ref. [3], while the group velocities for LA and TA branches are 15045 *m/s* and 10640 *m/s*, respectively. The Grüneisen parameters for LA and TA branches are 2.0 and 0.75, respectively [8].

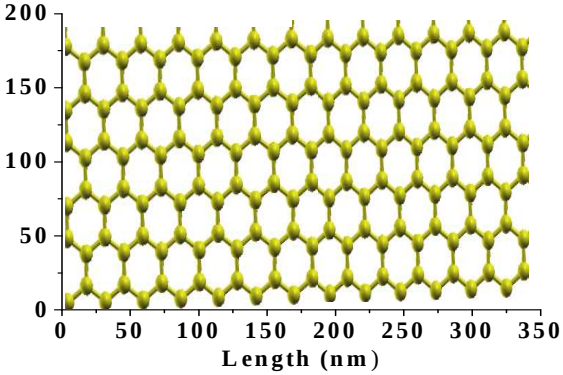

Figure 1: The schematic diagram for Graphen Nanoribbon (GNR).

In Figure 1, the atoms denoted with (yellow) circles at the ends are fixed to avoid the spurious global rotation of the GNRs in the our simulation [27]. We have also performed simulations regarding width and length conditions quantitatively. Out hypothesis is that thermal conductivity is limited and dependent on the finite length and width of GNRs.

Figure 2 shows the length dependence of thermal conductivity in GNRs with different edge roughness along with temperature effect. In the situation, we consider the width of GNRs to be 50 nm and that length ranges from 100 nm to 1050 nm. Results suggest that our calculated thermal conductivity is limited by the finite length of GNRs and corresponds to the value for graphene of macroscopic size. This is consistent with the phonon mean free path (MFP) in graphene extracted from the experiment (775 nm) [4] being approximately the same as the length (up to ~1000 nm) of the GNRs simulated in this study. It is noticeable that the length dependence of thermal conductivity in GNRs is controlled by the phonon-boundary scattering mechanism, while phonon mean free path (MFP) is controlled by the length of GNRs. It is observed in Figure 2 that thermal conductivity rapidly increases with length, as acoustic phonons with longer wavelengths become available for heat transfer.

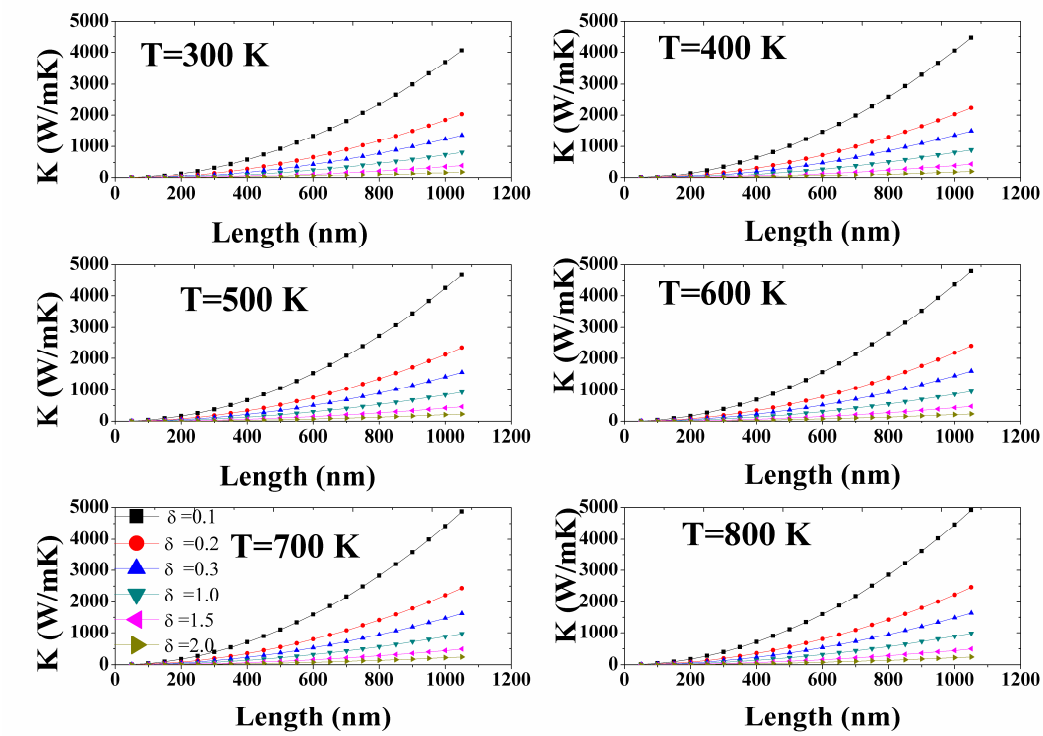

Figure 2: The length dependence of thermal conductivity of GNRs with different edge roughness along with temperature variations.

An increase in the GNRs length increases the number of phonons that experience lateral boundary scattering, resulting in MFP being dependent on both end and lateral boundary scattering. The finite value of thermal conductivity of GNRs results from the existence of diffuse phonon-boundary scattering. In the case of large edge roughness (δ = 2.0 nm), almost all phonons undergo a pure diffuse reflection at lateral boundaries, so the phonons diffuse normally and the thermal conductivity converges to a constant when the length of GNRs is longer than 700 nm, which is believed to be the phonon MFP in graphene. Thermal conductivity increases with increasing temperature as the number of scattered phonons increases. Temperature dependence deviates from 1/T law, particularly for small nanoribbons, due to the boundary restrictions on phonon MFP from graphene edges. This has correlations to heat transport of polycrystalline materials with similar restrictions on phonon MFP due to the boundaries.

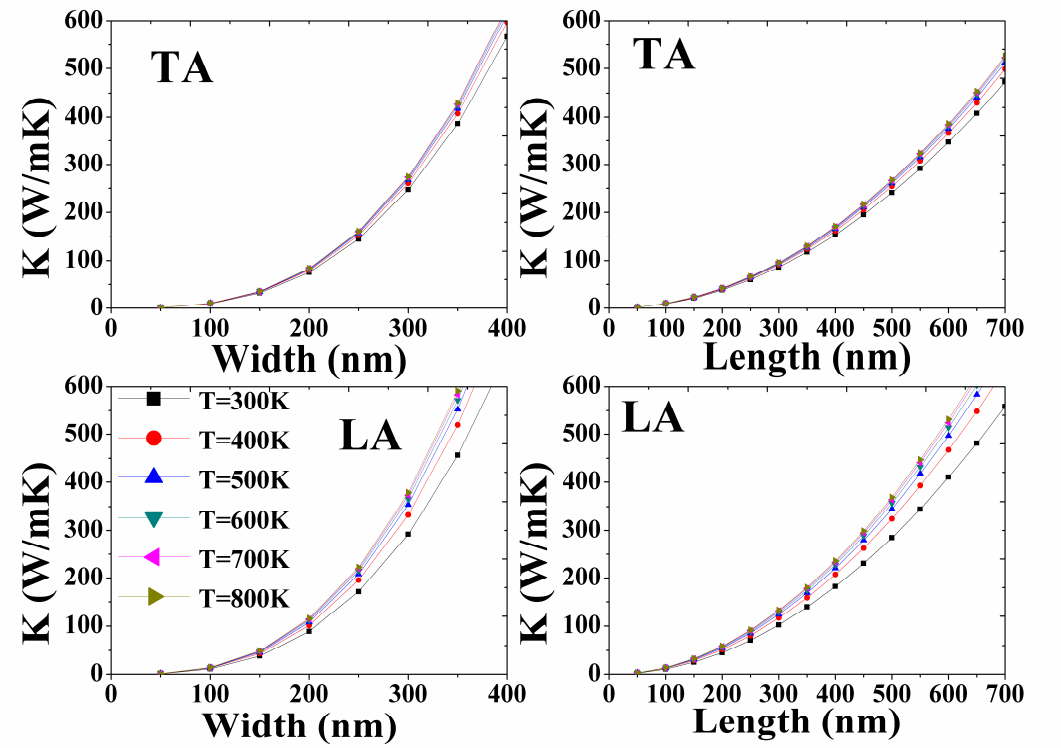

Figure 3: The width and length dependence of thermal conductivity of LA and TA branches in GNRs.

Figure 3 gives the width and length dependence of thermal conductivity of individual branch in GNRs at different temperatures from 300K to 800K. In this case, effective layer thickness is taken to be 0.35 nm. Thermal conductivity of LA and TA branches increases as the length of GNRs increases, indicating that longitudinal and transversal modes both positively contribute to the length dependence of thermal conductivity. On the other hand, the thermal conductivity of both branches almost converges with increasing temperature. The difference in length dependence of thermal conductivity between the in-plane branches (LA and TA) stems from the different phonon dispersion. Longitudinal modes have a greater energy dispersion and, thus, a greater distribution of phonon velocities. Higher velocities provide them larger phonon MFPs and larger MFPs of longitudinal modes give larger contribution to thermal conductivity. Relative influence to the thermal conductivity of individual branches is also length-dependent, as presented in Fig. 3.

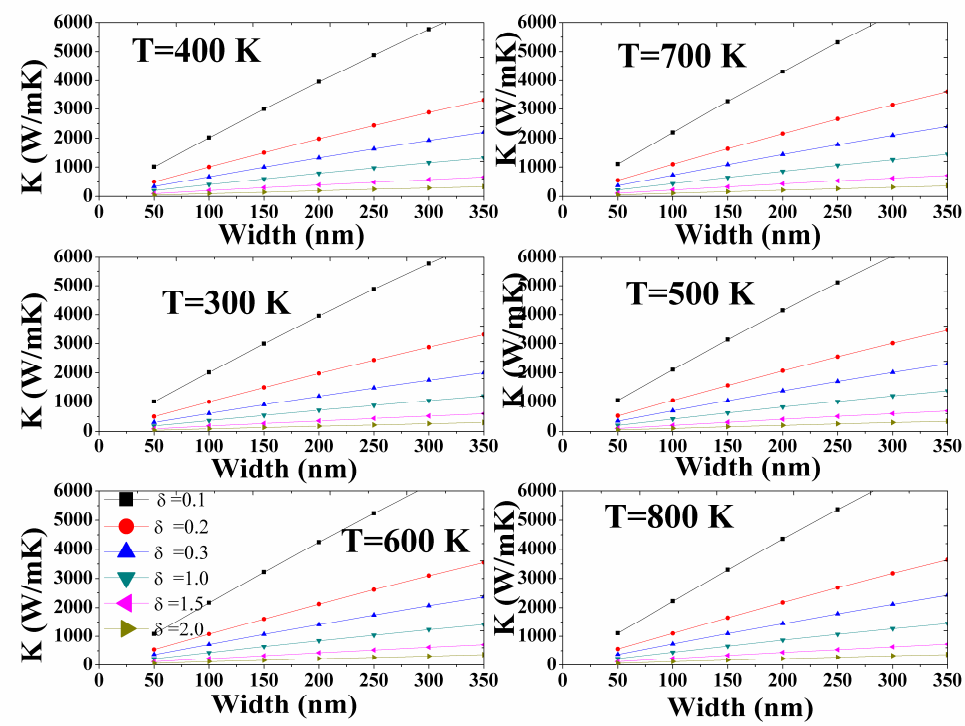

Figure 4: The width dependence of thermal conductivity of GNRs with different edge roughness along with temperature variations.

The width-dependence of thermal conductivity of GNRs is also determined along with edge roughness and temperature variations, as shown in Fig. 4. In the case of purely specular reflection at smooth lateral boundaries (δ=0), according to eqns (4)-(6), the averaged relaxation time of phonon-boundary scattering τ_B is only determined by the length of GNRs. Therefore, the thermal conductivity is governed by both factors, i.e. length and width under diffuse reflection conditions. Both dependences become more evident when the edge roughness is smaller.

We also observed a similar trend, as discussed by Han and Kim in their recent experiment [18], that at the charge neutrality point, a length-independent transport gap forms. The size of this gap is inversely proportional to the GNR width. In particular, we found that in this gap electrons are localized, and charge transport exhibits a transition between

thermally activated behavior at higher temperatures and variable range hopping at lower temperatures.

To more insight, the effect of edge rougness on graphene nanoribbon gives that the contribution of flexural phonons increases as the width decreases. The mechanism can be understood as when the width is smaller, the number of phonons that experience lateral boundary scattering is larger, indicating that the suppression of in-plane phonons is significantly stronger than that of out-of-plane phonons, which is also confirmed in the previous study of graphene phonon dispersion [18]. From this we can see that due to the small phonon group velocity, flexural phonons have a dominant contribution to the thermal conductivity of graphene whose length and width are not larger than one micron [31]. In other words, in GNRs whose width is much less than phonon MFP in graphene (about 800 nm), the mean free path of in-plane phonons is suppressed by diffuse phonon-boundary scattering at lateral boundaries of GNRs with rough edges, which enhances the contribution of flexual phonons to heat conduction in GNRs. Although the simulated GNRs have much smaller width with respect to that of graphene in experiments, we observed the strong size dependence in agreement with Refs. [4] and [5].

In conclusion, we have investigated a simple model for calculating the thermal conductivity of graphene nanoribbons of different widths, lengths and edge roughness. It explains the main features of pure 2D phonon transport in graphene nanoribbon, which distinguishes it from that of graphite. The diffuse phonon-boundary scattering suppresses the thermal conductivity of GNRs. The suppression of thermal conductivity by diffusive phonon-boundary scattering in TA branch is more remarkable than that in LA branch. When the edge roughness increases from 0 (purely specular reflection) to 2.0 nm (almost purely diffusive reflection for all phonons), the thermal conductivity of phonon modes decreases. Lengths and widths of graphene nanoribbons have significant influence on thermal conductivity. Our

model advocates that appropriate combinations of GNRs' length, width and edge roughness can imbue them with properties which will benefit their nano- and thermoelectric device applications. The model utilizes parameters which are responsible for the heat conduction of LA and TA phonon branches. The thermal conductivity calculated with our model gives results consistent with the *ab initio* theory of heat conduction in graphene and in excellent agreement with the experiments.

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Figure 1

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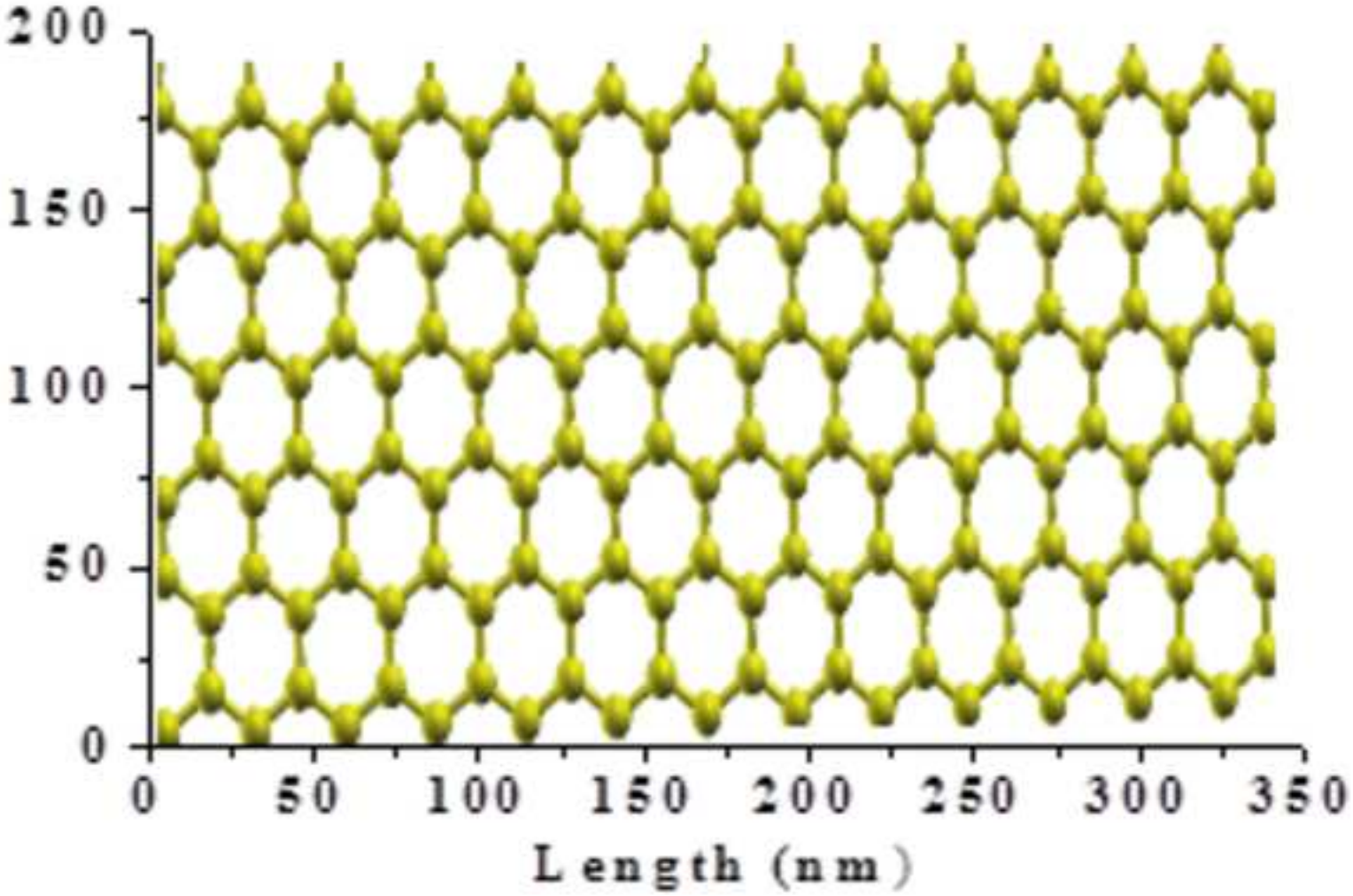

Figure 2

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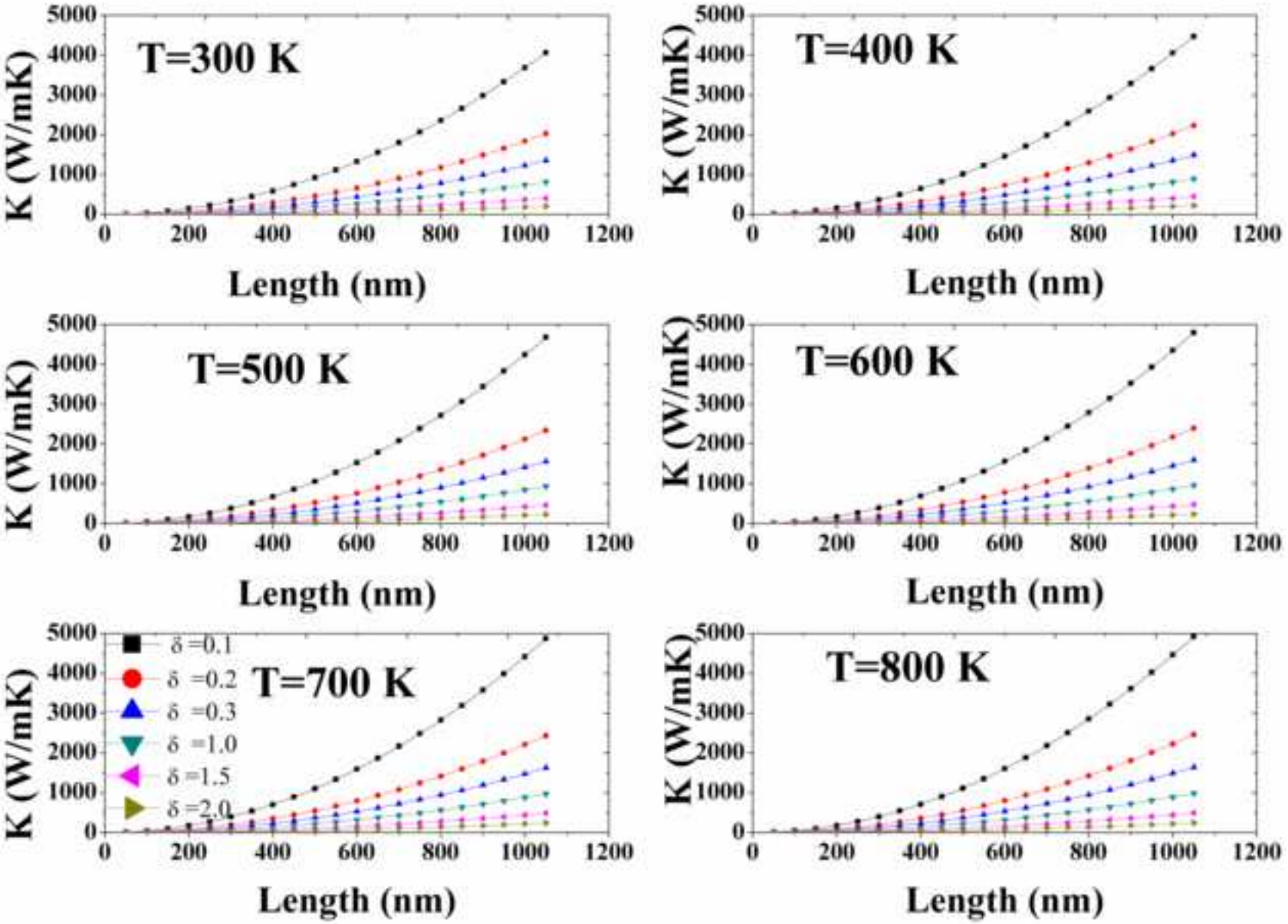

Figure 3

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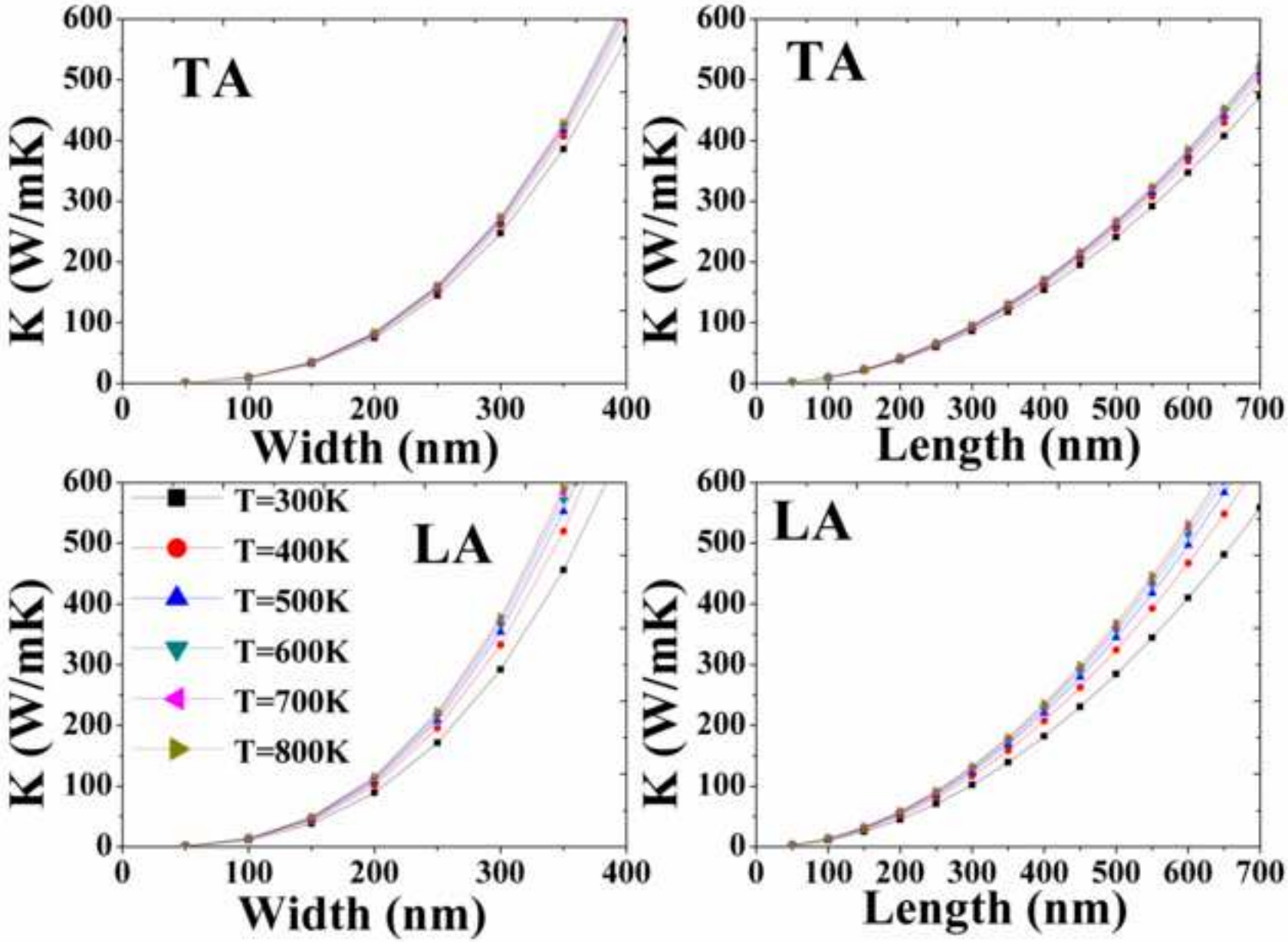

Figure 4

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