

Review

Phonons and thermal transport in graphene and graphene-based materials

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Abstract

A discovery of the unusual thermal properties of graphene stimulated experimental, theoretical and computational research directed at understanding phonon transport and thermal conduction in two-dimensional material systems. We provide a critical review of recent results in the graphene thermal field focusing on phonon dispersion, specific heat, thermal conductivity, and comparison of different models and computational approaches. The correlation between the phonon spectrum in graphene-based materials and the heat conduction properties is analyzed in details. The effects of the atomic plane rotations in bilayer graphene, isotope engineering, and relative contributions of different phonon dispersion branches are discussed. For readers' convenience, the summaries of main experimental and theoretical results on thermal conductivity as well as phonon mode contributions to thermal transport are provided in the form of comprehensive annotated tables.

Keywords: graphene, phonons, thermal transport, specific heat

(Some figures may appear in colour only in the online journal)

1. Introduction

Monoatomic sheet of sp^2 hybridized carbon atoms—graphene—demonstrates unique electrical [1–3], thermal [4–6], optical [7, 8] and current fluctuation [9–11] properties owing to its quasi two-dimensional (2D) electron and phonon transport. The ultra-high thermal conductivity of graphene is beneficial for its proposed electronic applications, and it serves as a foundation for numerous possible thermal management applications, e.g. as heat spreaders for transistors and light emitting diodes, and fillers in thermal interface materials for electronic chips [12–19]. There have been several review papers devoted to thermal transport in graphene and

graphene-based materials [6, 18, 20–25]. However, the *graphene thermal field* is still in the period of explosive growth. Many new theoretical and experimental results have been reported in the past few years. A number of issues are still awaiting their conclusive resolution. Some new fundamental science questions have been asked. The discussion of the most recent results in the overall context of graphene thermal field is required. In this paper, we review theoretical models for phonons and thermal transport in graphene and graphene nanoribbons (GNRs), describe different experimental techniques for measuring phonon energies and thermal conductivity, and discuss the relative phonon branches contribution to thermal conductivity.

2. Phonons in graphene and graphene nanoribbons

Single-layer graphene (SLG) possesses the honeycomb crystal lattice with two basis vectors $\bar{a}_1 = a(3, \sqrt{3})/2$, and $\bar{a}_2 = a(3, -\sqrt{3})/2$, where $a = 0.142 \text{ nm}$ is the distance between two nearest carbon atoms (see figure 1) [26]. The rhombic unit cell of SLG, shown as a dashed region in figure 1, contains two carbon atoms from different Bravais sublattices. In figure 1, the atoms from the first sublattice are marked as ‘white’, while atoms from the second one—as ‘black’ atoms. There are six phonon branches in SLG: in-plane longitudinal acoustic (LA) and optic (LO), in-plane transversal acoustic (TA) and optic (TO) and out-of-plane acoustic (ZA) and optic (ZO). The displacement vector \vec{U} of the in-plane phonon modes has only the in-plane components, i.e. $\vec{U} = (U_x, U_y, 0)$, while \vec{U} of the out-of-plane modes is directed along Z -axis: $\vec{U} = (0, 0, U_z)$. Here we assume that axis X and Y of Cartesian coordinate system are in the plane of graphene layer while axis Z is perpendicular to it.

The phonon energies are the key parameters for understanding the phonon processes in graphene-based materials. Therefore, significant efforts have been directed at developing various theoretical models for description of phonons in SLG, few-layer graphene (FLG) and graphene nanoribbons [26–64]. These models can be divided into three groups: (i) dynamic models (DMs) of the lattice vibrations [26–46], (ii) elastic continuum models (ECMs) [47–54] and (iii) *ab initio* density functional theory (DFT) models with the local density approximation (LDA) or generalized gradient approximation (GGA) [43, 55–64]. The first group includes Born-von Karman models with fourth- and fifth-nearest neighbor interactions [27, 28, 31–33, 36–38] and valence-force field models [26, 29, 30, 34, 35], as well as models employing different potentials of the interatomic interaction: Tersoff, Brenner, Lennard-Jones or reactive empirical-bond-order potentials [39–46]. In the framework of DMs, the phonon energies are calculated by solving the system of equations of motion for atoms:

$$\omega^2 u_\alpha^k(\vec{q}) = \sum_{k', \beta} D_{\alpha\beta}^{kk'} u_\beta^{k'}(\vec{q}); \quad \alpha, \beta = x, y, z,$$

$$D_{\alpha\beta}^{kk'} = \frac{1}{m_C} \sum_{n'} \Phi_{\alpha\beta}(k, n; k', n') \exp(i\vec{q}(\bar{a}_n - \bar{a}_{n'})), \quad (1)$$

where $u_\alpha^k [u_\alpha^{k'}]$ is a component of the displacement vector for an atom $k [k']$ from the unit cell $n [n']$, $\bar{a}_n [\bar{a}_{n'}]$ is the lattice vector of a unit cell $n [n']$, ω is the phonon frequency, \vec{q} is the phonon wave vector, $\Phi_{\alpha\beta}(k, n; k', n')$ is the tensor of the second-order interatomic-force constants (IFCs), m_C is a mass of a carbon atom and $k = 1, 2$. The summation in equation (1) is performed over all unit cells n' and over all atoms from the unit cell $k' = 1, 2$. The interatomic force-constant tensor strongly depends on the model used, and on the types of the interatomic interactions considered in the model. Usually DMs are characterized by a set of the fitting parameters, which are determined from comparison with the experimental data. If a set of parameters is chosen in an optimal way the dynamic

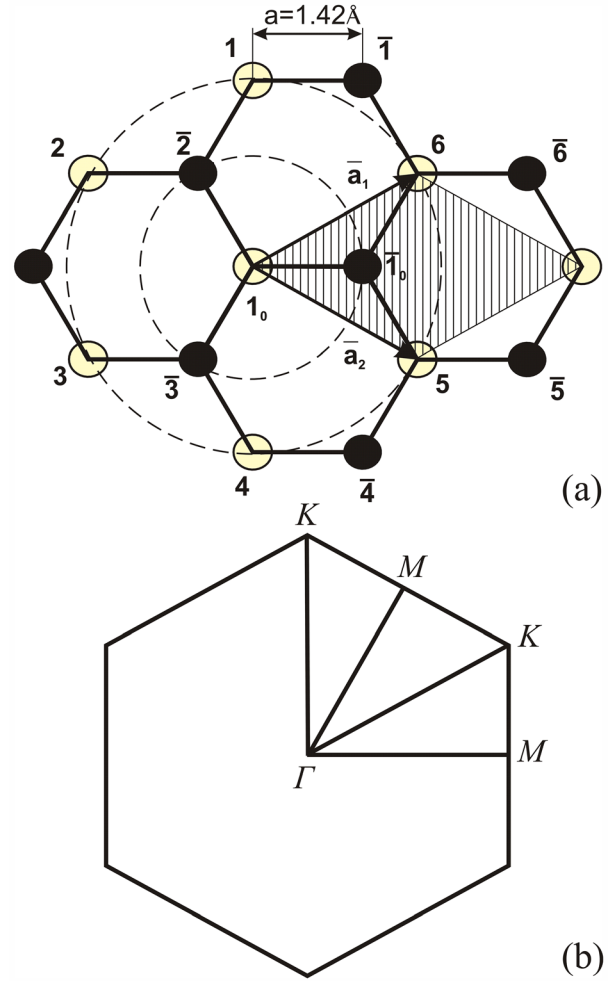


Figure 1. Schematic view of crystal lattice (a) and Brillouin zone (b) for single layer graphene. The figure is reprinted from [26], copyright 2009 with permission from the American Physical Society.

models of the lattice vibrations describe the phonon frequencies with high accuracy. An important difference among DMs is the number of the fitting parameters used. The number of such parameters reported to date varied from 5 [27] to 23 [32].

The phonon dispersion in SLG and AB-stacked bi-layer graphene (AB-BLG) is shown in figure 2 along ΓM direction of the Brillouin zone. These dispersion relations were calculated using the Born–von Karman approach for the intralayer carbon–carbon interactions [36] and the spherically symmetric interatomic potentials for the interlayer interactions [36–38]. The red triangles show the experimental frequencies from [28]. At small q in the vicinity of Γ -point, the LA and TA branches are almost linear with q : $\omega_{\text{LA,TA}} \sim q$ while the ZA branch demonstrates quadratic dependence $\omega_{\text{ZA}}(q) \sim q^2$.

In the framework of the elastic continuum models, the few-layer graphene is approximated as a stack of equally spaced and interacting elastic sheets. The system of equations of motion for the elastic vibrations in each sheet is given by [48]:

$$D\Delta^2 w_i + \rho h \frac{\partial^2 w_i}{\partial t^2} = q_i, \quad i = 1, 2, \dots, N \quad (2)$$

where N is the number of sheets, D is the bending stiffness of each sheet, ρ is the mass density, h is the sheet thickness, q_i is

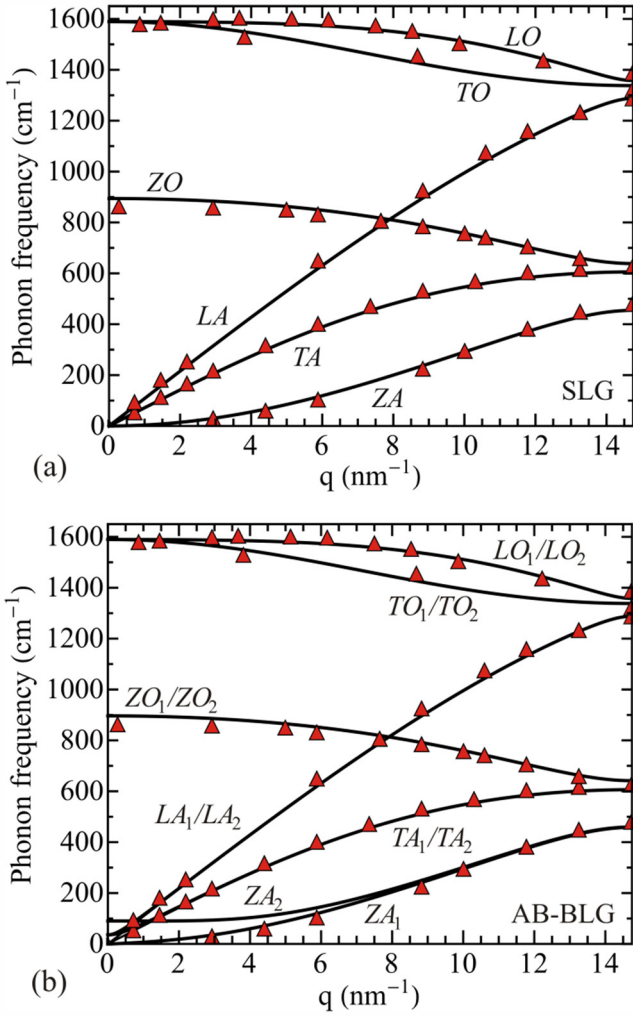


Figure 2. Phonon dispersions in (a) single layer graphene and (b) AB-stacked bilayer graphene, plotted along ΓM direction of Brillouin zone. The phonon energies were calculated using the BvK model of the lattice vibrations. The figure is adopted from [38], copyright 2015 with permission from the Royal Society of Chemistry.

the pressure applied to an atomic sheet i due to the interlayer van der Waals (vdW) interactions, w_i is the deflection of i th sheet and $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2$. For infinitesimal vibrations, the pressure due to the vdW interactions can be assumed in the following form: $q_i = w_i \sum_{j=1}^N c_{ij} - \sum_{j=1}^N w_j c_{ij}$, where c_{ij} are the vdW interaction coefficients [48]. Solving equation (2) by using 2D propagating waves, the following equations for phonon frequencies were derived in [48]:

$$\left(D \left[\left(\frac{\pi m}{L_x} \right)^2 + \left(\frac{\pi n}{L_y} \right)^2 \right]^2 - \sum_{j=1}^N c_{ij} - \rho h \omega^2 \right) u_i + \sum_{j=1}^N c_{ij} u_j = 0, \quad i = 1, 2, \dots, N, \quad (3)$$

where L_x is the sheet length, L_y is the sheet width, m and n are the half wave numbers in the sheet plane.

Employing the semi-continuum model from [65], Nishira and Ivata [47] derived the analytical expressions for the phonon frequencies in graphite:

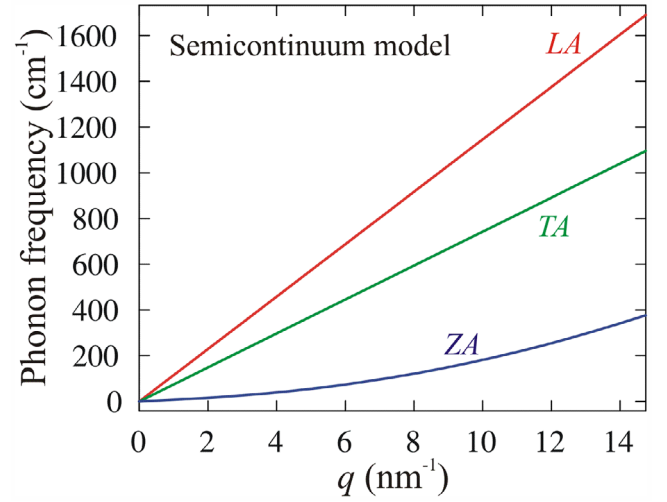


Figure 3. Phonon dispersion in single layer graphene, calculated in the framework of the elastic continuum approach.

$$\begin{aligned} \omega_{LA}^2 &= v_l^2(q_x^2 + q_y^2) + \frac{4\zeta}{c^2} \sin^2\left(\frac{cq_z}{2}\right), \\ \omega_{TA}^2 &= v_t^2(q_x^2 + q_y^2) + \frac{4\zeta}{c^2} \sin^2\left(\frac{cq_z}{2}\right), \\ \omega_{ZA}^2 &= b^2(q_x^2 + q_y^2)^2 + 4\mu^2 \sin^2\left(\frac{cq_z}{2}\right) + \zeta(q_x^2 + q_y^2). \end{aligned} \quad (4)$$

In equation (4) v_l/v_t is the longitudinal/transverse in-plane velocity, correspondingly, c is the interlayer spacing, b is the bending elastic parameter, $\zeta = c_{44}/\rho$ and $\mu = \sqrt{c_{33}/(\rho c^2)}$. In the case of single-layer graphene, $q_z = 0$ and the phonon frequencies are given by:

$$\begin{aligned} \omega_{LA}^{SLG} &= v_l \sqrt{(q_x^2 + q_y^2)} = v_l q, \\ \omega_{TA}^{SLG} &= v_t \sqrt{(q_x^2 + q_y^2)} = v_t q, \\ \omega_{ZA}^{SLG} &= \sqrt{b^2(q_x^2 + q_y^2)^2 + \zeta(q_x^2 + q_y^2)}. \end{aligned} \quad (5)$$

In figure 3 we show the dispersion for the LA, TA and ZA phonon branches along the ΓM direction of BZ, calculated from equation (5). The parameters $v_l = 21.6 \text{ km s}^{-1}$, $v_t = 14.0 \text{ km s}^{-1}$, $\zeta = 1.88 \times 10^{10} \text{ cm}^2 \text{ s}^{-2}$ and $b = 3.13 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ were taken from [47]. In the semi-continuum model $\omega_{LA}^{SLG}, \omega_{TA}^{SLG} \sim q$ while $\omega_{ZA}^{SLG} \sim q^2$ over the entire Brillouin zone resulting in an overestimation of the LA/TA phonon frequencies for $q > 8 \text{ nm}^{-1}$ and underestimation of ZA phonon frequencies for $q > 4 \text{ nm}^{-1}$ in comparison with both experimental and BvK model results (see figure 2). The deviation of the ZA phonon branch from the parabolicity (see figure 2) strongly affects the phonon density of states and specific heat [38].

The *ab initio* DFT-based models are a powerful tool for investigation of phonon processes in graphene materials. Nevertheless, employment of these models requires careful checking of the obtained results. Possible numerical inaccuracies in calculating the *ab initio* IFCs may strongly influence the phonon dispersions, and even lead to deviation from the q^2 dependence of the ZA branch at small q [66]. To resolve

this issue, in [67] the acoustic sum rules were numerically reinforced.

An increase in the number of graphene atomic layers results in the larger unit cell volume and the number of atoms in the unit cell. The unit cell of the n -layer Bernal stacked graphene contains $2n$ atoms, therefore $6n$ phonon branches appear in the energy spectrum of n -layer graphene sample.

The evolution of the phonon energy spectra near center of the BZ when one goes from SLG to AB-bilayer graphene to ABA-trilayer graphene (ABA-TLG) is illustrated in figure 4. Additional phonon branches of AB-BLG and ABA-TLG, indicated in figure 4 as LA_2 , LA_3 , TA_2 , TA_3 , ZA_2 and ZA_3 , are characterized by non-zero frequencies at Γ point. These frequencies strongly depend on weak interlayer vdW forces, therefore their values vary from one theoretical model to another. Employment of the Lennard-Jones potential for modeling of vdW interlayer interaction in graphite results in lower frequencies of LA/TA branches, calculated along ΓA direction of the BZ, as compared with the experimental data [37]. Authors of [37, 38] proposed to model interlayer interaction by another type of spherically symmetric interatomic potential instead of Lennard-Jones potential. The phonon dispersions in graphite calculated within this approach were in a good agreement with the experimental curves [37].

The phonon modes in twisted bilayer graphene (TBLG) were theoretically studied in [36]. When two graphene layers are placed on top of each other they can form a Moire pattern [68–70]. In this case, one layer of carbon atoms is rotated relative to another layer by a specific angle. The size of the unit cell in TBLG is larger than in AB-BLG and depends strongly on the rotational angle Θ . Therefore the number of phonon branches also depends on Θ . In figure 5 we show the phonon dispersions calculated along ΓK direction of the BZ in TBLG with $\Theta = 21.8^\circ$. The Brillouin zone of TBLG with $\Theta = 21.8^\circ$ is by a factor of seven smaller than the BZ of AB-BLG. Therefore, the *hybrid folded* phonon branches appear in twisted bilayer graphene resulting from mixing of different directions from un-rotated BLG BZ [36]. The twisting also slightly affects the phonon frequencies in TBLG due to modification of the weak vdW interlayer interaction.

The peculiarities of the phonon energy spectra in graphene reveal themselves in the phonon density of states (PDOS) and phonon specific heat. The 2D phonon density of states is given by [38]:

$$g(\omega) = \sum_s g_s(\omega); \quad g_s(\omega) = \frac{1}{4\pi^2} \sum_{q_x(s,\omega)} \sum_{q_y(s,\omega,q_x)} \frac{\Delta q_x}{|v_y(q_x, q_y, s)|}. \quad (6)$$

Here, s numerates phonon branches (polarizations), $g_s(\omega)$ is the polarization-dependent phonon density of states, q_x and q_y are components of the 2D phonon wave vector, $v_y = \partial\omega/\partial q_y$ is the y -component of the phonon group velocity, Δq_x is the interval between two neighboring q_x points. The dependence of PDOS in SLG (solid curves) and AB-BLG (dashed curve) on phonon frequency is presented in figure 6. The contribution of different phonon branches LA (green), TA (blue), ZA (red) and ZO (magenta) are also shown. The PDOS peaks at 452, 605 and 638 cm^{-1} correspond to ZA, TA and

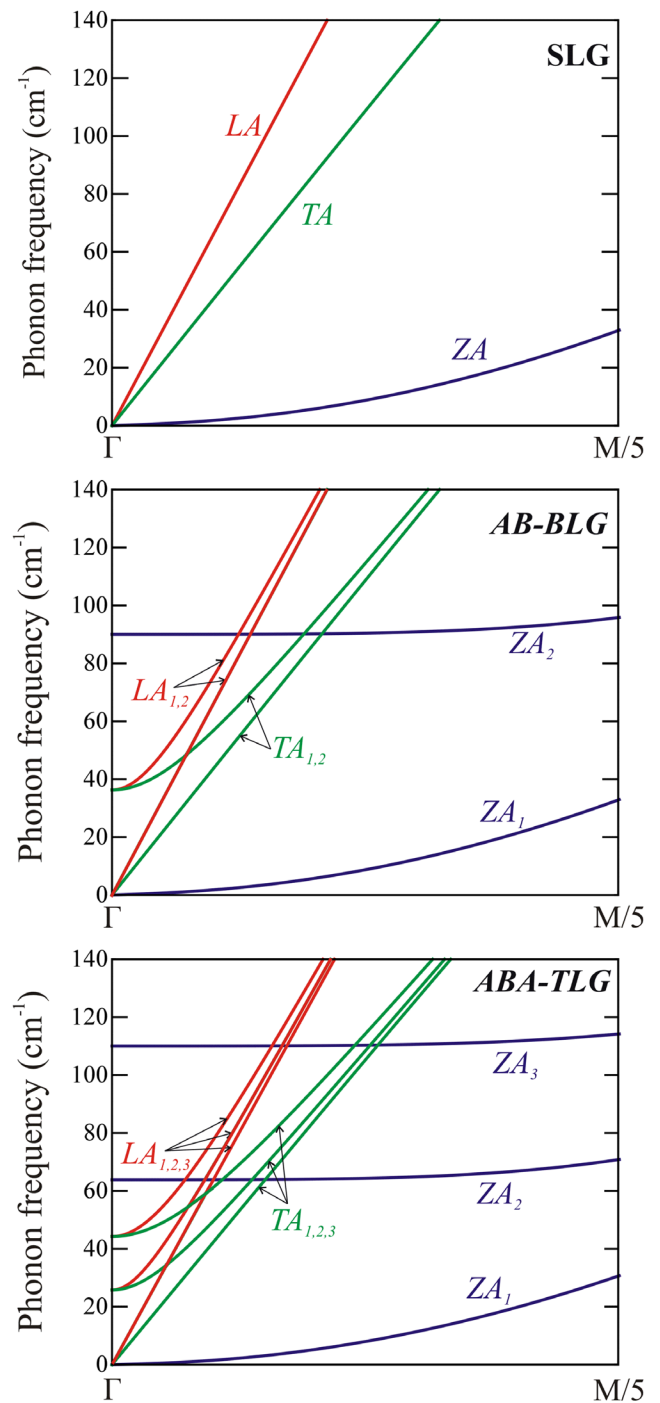


Figure 4. Phonon dispersion in single layer graphene, AB-bilayer graphene and ABA-three-layer graphene, plotted along ΓK direction near the center of Brillouin zone. The phonon energies were calculated using the BvK model of the lattice vibrations.

ZO phonon branches at BZ edge, correspondingly; the LA peak at $\sim 1192 \text{ cm}^{-1}$ is associated with the low-velocity LA phonons from different directions near BZ edge; the peak at 889 cm^{-1} is related to ZO phonon at Γ point and TO and LO phonons at BZ center and BZ edge are responsible for peaks at 1350 and 1585 cm^{-1} . The peak at 91 cm^{-1} of AB-BLG PDOS, which is absent in SLG, is related to ZA_2 phonons at Γ -point.

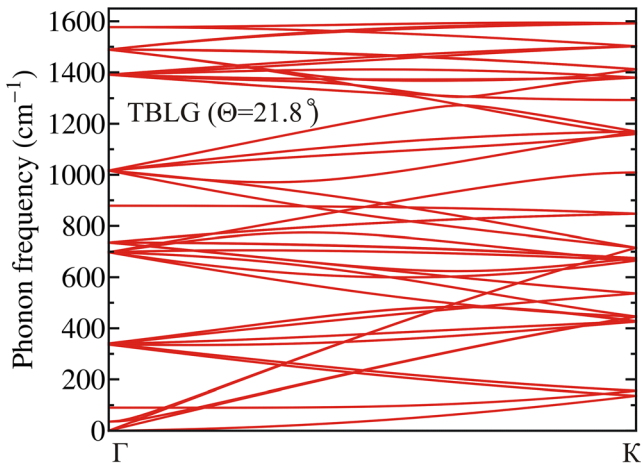


Figure 5. Phonon dispersion in twisted bilayer graphene with the twisting angle 21.8° . The figure is adopted from [37], copyright 2014 with permission from the American Institute of Physics.

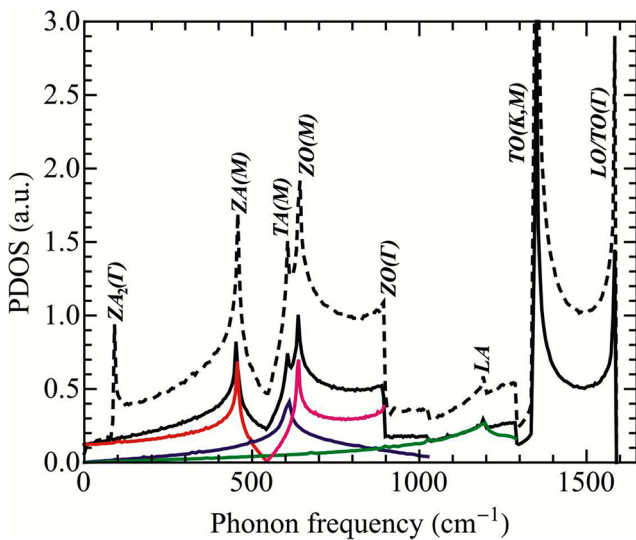


Figure 6. Total phonon density of states in SLG (solid black) and AB-BLG (dashed black), and contribution from ZA (red), TA (blue), ZO (magenta) and LA (green) phonon branches. PDOS is calculated using the phonon dispersion obtained within the BvK model of the lattice vibrations. The figure is reprinted from [38], copyright 2015 with permission from the Royal Society of Chemistry.

Theoretical studies of the phonon specific heat c_v in SLG were carried out in [37, 38, 52, 71]. Authors of [52, 71] used a simple model of phonon dispersions in graphene: parabolic ZA dispersion $\omega_{ZA} \sim q^2$ and linear LA/TA dispersions $\omega_{LA,TA} \sim q$ over entire Brillouin zone. In this case, the low-temperature specific heat is proportional to T for ZA modes and to T^2 for LA/TA modes. The linear dependence of total specific heat on temperature $c_v \sim T$ was reported in [71] for $T < 100$ K. The slight deviation from the linear T dependence due to contribution from LA and TA phonons was obtained in [52]: $c_v \sim T^{1.1}$. However more rigorous model of phonon specific heat in SLG, which takes into account both anisotropy of phonon dispersions and non-parabolicity of ZA branch for $\omega > 100 \text{ cm}^{-1}$, shows that the deviation from linear T dependence is stronger for $T > 35$ K: $c_v \sim T$ for $T \leq 15$ K; $c_v \sim T^{1.1}$ for $15 \text{ K} < T \leq 35$ K; $c_v \sim T^{1.3}$ for

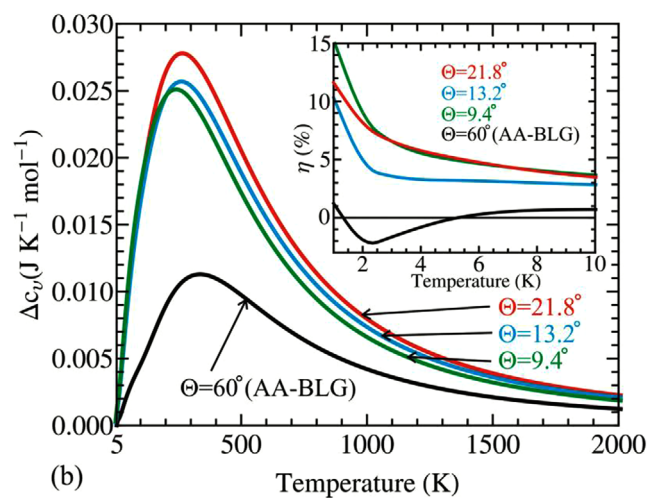
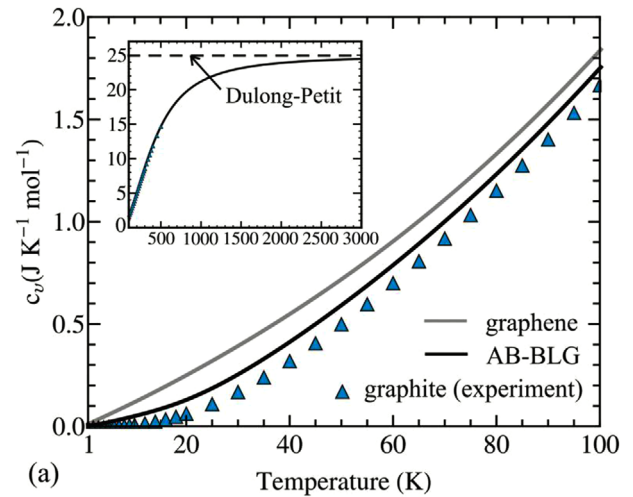


Figure 7. Temperature dependence of the phonon specific heat in graphite, SLG, AB-BLG and TBLG. The figure is adopted from [37], copyright 2014 with permission from the American Institute of Physics.

$35 \text{ K} < T \leq 70 \text{ K}$ and $c_v \sim T^{1.6}$ for $75 \text{ K} < T \leq 240 \text{ K}$ [37, 38]. In bilayer graphene the low-temperature specific heat scales with T as $c_v \sim T^n$, where $n = 1.3$ for AA- or AB-BLG and $n = 1.6$ for TBLG with $\Theta = 21.8^\circ$ [38].

The temperature dependence of the specific heat in SLG and AB-BLG is depicted in figure 7(a). The experimental points for graphite from [47] are also shown by the blue triangles. The difference between the heat capacities in graphite, SLG and BLG decreases with increasing temperature, and for $T > 2500$ K all heat capacities approach the classical Dulong-Petit limit $c_v = 24.94 \text{ J K}^{-1} \text{ mol}^{-1}$. The dependence of c_v in TBLG on the rotational angle is illustrated in figure 7(b). In this figure we plot a difference between the specific heats in AB-BLG and TBLG $\Delta c_v = c_v(\text{AB-BLG}) - c_v(\text{TBLG})$ as a function of temperature for different Θ . The change in specific heat due to twisting is relatively weak for temperatures $T > 20$ K. Nevertheless at very small temperature $T \sim 1$ K, the relative difference between specific heat in AB-BLG and TBLG $\eta = \Delta c_v / c_v(\text{AB-BLG}) \times 100\%$ achieves 10–15% (see inset to figure 7(b)) due to changes in the frequencies of ZA

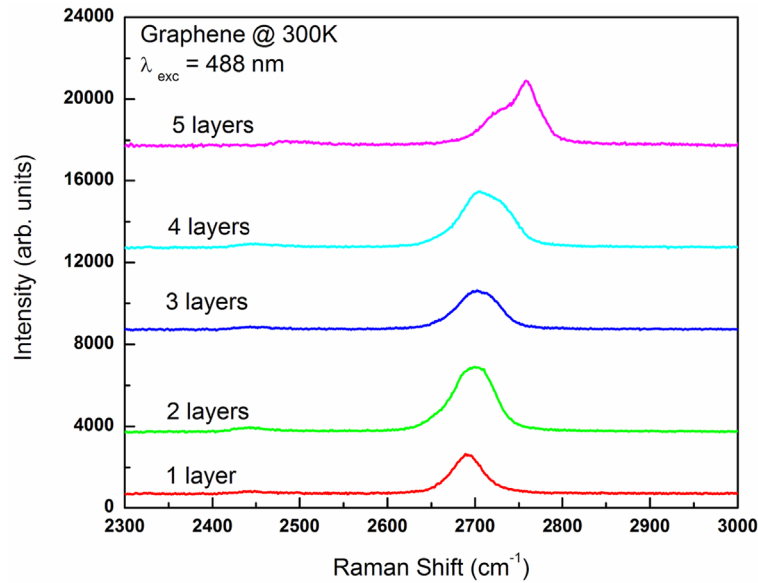


Figure 8. Room-temperature Raman spectrum of graphene and few-layer graphene showing the 2D-band spectral region. Note that the position and shape of the 2D peak depend on the number of atomic planes. The figure is reprinted from [74], copyright 2007 with permission from the American Chemical Society.

phonons. Although the general trends in the phonon dispersion in graphene are well described by the majority of theoretical models the peculiarities of phonon branches as well as phonon energies in the high symmetry points of the Brillouin zone vary from one model to another [20]. This discrepancy is one of the reasons for different values of the phonon scattering rates and thermal conductivity predicted by different theoretical approaches [20].

The experimental investigations of phonon modes in graphite, single- and few-layer graphene were carried out using inelastic x-ray scattering [28, 56], inelastic electron tunneling spectroscopy [72] and Raman spectroscopy [73–89]. The earlier Raman studies of SLG revealed three different phonon bands in graphene: G-, D- and 2D-band. The G-band near 1485 cm^{-1} is the first-order Raman peak associated with scattering of in-plane optical phonons of BZ Γ -point. Scattering of two TO phonons around K -point of BZ gives rise to 2D-band, i.e. the second-order Raman peak in the range $2500\text{--}2800\text{ cm}^{-1}$. More recent Raman studies observed peaks associated with the shear phonons in few-layer graphene [78–82] and folded phonons in twisted few-layer graphene [69, 70, 83–89]. The dependence of the Raman 2D peak spectral position and shape on number of carbon atomic layers is shown in figure 8.

The Kohn anomalies (KA) in graphene and GNRs, i.e. discontinuity in the derivatives of the phonon branches over wave vector at the certain points of BZ, have been studied in [90–94]. Using DFT with GGA, Piscanec *et al* [90, 91] found two Kohn anomalies in graphene: KA of LO phonon mode at Γ -point and KA of TO phonon mode at K -point. This result was confirmed using the force constant approach [92]. Forster *et al* [94] demonstrated both theoretically and experimentally that frequencies of the highest optical-phonon branch in supported graphene depend on the external screening by the dielectric substrate. As a result, Kohn anomalies in

supported graphene can be tuned by the substrate due to the reduction of the electron–phonon interaction [93]. Sasaki *et al* [93] have theoretically shown that in GNRs exist KA of LO phonons only while the frequency derivatives of TO phonons are continuous.

3. 2D thermal transport in graphene-based materials

In this section we review theoretical and experimental results pertinent to the phonon thermal transport in graphene—based materials, focusing on the most recent reports. These findings are discussed in details and compared with earlier results.

3.1. Experimental investigations of thermal transport in graphene and graphene-based materials

The first experimental measurements of thermal conductivity of graphene were conducted at the University of California—Riverside in 2008 [4, 5] using non-contact Raman optothermal method. In this technique the central part of graphene layer suspended over a trench was heated by the laser light, resulting in local temperature rise and corresponding frequency shift of Raman G peak. Measuring this frequency shift allows one to extract the temperature profile of local heated area. The measured room temperature (RT) values of thermal conductivity (TC) were in the range $\kappa = 3000\text{--}5400\text{ W m}^{-1}\text{ K}^{-1}$ and exceeded the thermal conductivity of the best bulk thermal conductors: highly—oriented pyrolytic graphite (HOPG) and diamond [6]. In figure 9 we illustrate the linear dependence of Raman G peak shift on the temperature, which is used for extraction of the temperature in the Raman optothermal method.

The latter independent measurements of thermal conductivity in graphene were performed using different techniques: Raman optothermal, electrical self-heating and T-bridge

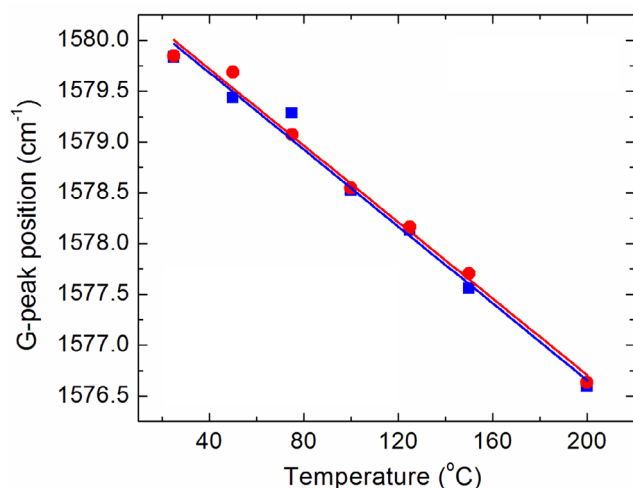


Figure 9. Raman G peak as a function of the sample temperature. The measurements were carried out under the low excitation power to avoid local heating while the temperature of the sample was controlled externally. Note an excellent linear fit for the examined temperature range. The figure is reprinted from [118], copyright 2014 with permission from the American Chemical Society.

methods. Using Raman optothermal technique Cai *et al* [95] found that thermal conductivity of suspended chemical vapor deposited (CVD) graphene is $\sim 2500 \text{ W m}^{-1} \text{ K}^{-1}$ at 350 K and $\sim 1400 \text{ W m}^{-1} \text{ K}^{-1}$ at 500 K. Other optothermal studies revealed TC in suspended CVD graphene in the range from 1500 to 5000 $\text{W m}^{-1} \text{ K}^{-1}$ [96]. Faugeras *et al* [97] also employed Raman optothermal method for measurements of thermal conductivity of suspended graphene in Corbino membrane geometry and found $\kappa \sim 600 \text{ W m}^{-1} \text{ K}^{-1}$ at $T \sim 660 \text{ K}$. As in conventional materials the thermal conductivity decreases with temperature owing to increasing phonon–phonon scattering.

The high-temperature thermal transport in suspended exfoliated and CVD graphene was experimentally studied by Dorgan *et al* [98] within electrical self-heating method. For this study authors fabricated 15 devices with suspended exfoliated or CVD graphene. Average TC of exfoliated and CVD graphene samples were similar $\kappa \sim 310 + 200/ - 100 \text{ W m}^{-1} \text{ K}^{-1}$ at $T = 1000 \text{ K}$. The RT TC was in the range 2000–3800 $\text{W m}^{-1} \text{ K}^{-1}$ with the average value of 2500 $\text{W m}^{-1} \text{ K}^{-1}$, which is in a good agreement with previous experimental results [4, 5, 95, 96]. Dorgan *et al* [98] also found that high-temperature TC in graphene demonstrates steeper decrease with temperature $\kappa \sim T^{-1.7}$ than that in graphite. This effect was attributed to the stronger second-order three phonon scattering in graphene. The lower values of thermal conductivity were found in the supported graphene due to coupling of graphene phonon modes to substrate modes and additional phonon scattering on the graphene–substrate interface [99]. The thermal conductivity of graphene encased in other materials is also substantially smaller than that in SLG [100]. The reasons for TC drop are similar to the supported graphene case: coupling of graphene phonons to phonons from another material and phonon scattering on interfaces and disorder. The dependence of the thermal conductivity of suspended graphene on the

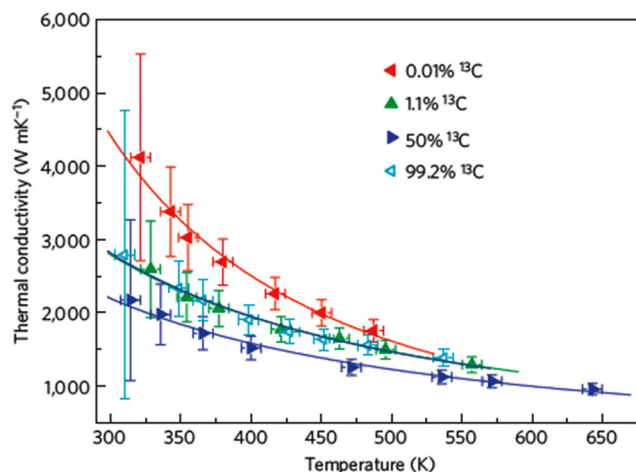


Figure 10. Thermal conductivity of suspended graphene with different concentration of ^{13}C isotope. The figure is reprinted from [103], copyright 2012 with permission from the Nature Publishing Group.

number of atomic layers n was studied in [34]. It was established that thermal conductivity decreases with increasing of n from 1 to 4 and for $n = 4$ approaches the value of TC in HOPG. The polymeric residues, often presenting on graphene surface influence both TC values [101] and TC dependence on the number of atomic layers [102]. The unusual dependence of the intrinsic thermal conductivity of graphene on the number of atomic planes was discussed in details in [6].

The isotope scattering and scattering on crystal lattice defects are important parameters, which affect the graphene thermal conductivity. Chen *et al* [103] reported on experimental study of isotope effect on thermal properties of graphene, using the Raman optothermal method. The increase of ^{13}C isotope concentration N_{isot} led to the strong suppression of the thermal conductivity from $\sim 2800 \text{ W m}^{-1} \text{ K}^{-1}$ for $N_{\text{isot}} = 0.01\%$ to $\sim 1600 \text{ W m}^{-1} \text{ K}^{-1}$ for $N_{\text{isot}} = 50\%$ at $T \sim 380 \text{ K}$ (see figure 10).

Malekpour *et al* [104] investigated thermal conductivity of suspended SLG as a function of the density of crystal lattice defects N_d , introduced by low-energy electron beam irradiation. It was shown that RT TC decreases from $\sim 1800 \text{ W m}^{-1} \text{ K}^{-1}$ to $\sim 400 \text{ W m}^{-1} \text{ K}^{-1}$ with increase of N_d from $2.0 \times 10^{10} \text{ cm}^{-2}$ to $1.8 \times 10^{11} \text{ cm}^{-2}$. An intriguing saturation of thermal conductivity dependence on N_d was revealed at higher N_d [104].

Li *et al* [105] also employed Raman optothermal technique for investigation of thermal transport in twisted bilayer graphene. The authors found that in a wide range of examined temperatures, from 300 K to 750 K, the TC in TBLG is smaller than both in SLG and AB-BLG (see figure 11). The thermal conductivity of twisted bilayer graphene is by a factor of two smaller than that in SLG and by a factor of ~ 1.35 smaller than that in AB-BLG near the room temperature. The drop of TC was explained by emergence of many additional hybrid folded phonons in TBLG resulting in more intensive phonon scattering [105].

Experimental studies [106–108] reported on strong dependence of thermal conductivity in graphene and GNRs

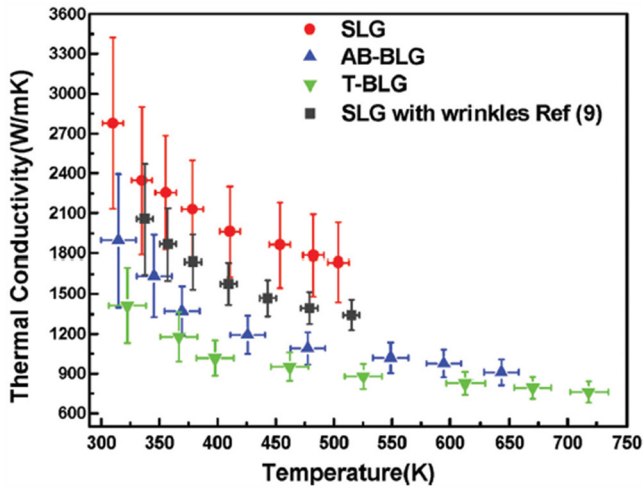


Figure 11. Thermal conductivity of suspended single-layer graphene, AB-bilayer graphene and twisted bilayer graphene as a function of temperature. The figure is reproduced from [105], copyright 2014 with permission from the Royal Society of Chemistry.

on the sample size: length or width. Xu *et al* [107] carried out measurements of thermal conductivity in suspended CVD single-layer graphene, using the electro-thermal bridge method and observed the logarithmic dependence of TC on the sample length L : $\kappa \sim \log(L)$ for examined range of L between 700 nm and 9 μm . Although different thermal resistivity of samples with different L may have affected the reported results, it is interesting to note that the obtained $\kappa \sim \log(L)$ dependence of thermal conductivity was in agreement with earlier theoretical predictions made for graphene [109–111] and pure 2D lattices [112, 113].

Bae *et al* [106] found that RT TC in GNRs with length $L \approx 260$ nm drops from 230 to 80 $\text{W m}^{-1} \text{K}^{-1}$ with decrease of GNRs width W from 130 to 45 nm, respectively, due to enhancement of edge roughness scattering. More general, the authors predicted that in GNRs with L and W larger than phonon MFP λ , the thermal transport is diffusive. In GNRs with $L \sim \lambda$ and $W \gg \lambda$, the transport is quasi-ballistic, while in GNRs with $L \sim \lambda$, $W \sim \lambda$ and $L > W$ the transport is diffusive due to phonon edge roughness scattering. These findings are in a qualitative agreement with theoretical results reported for micrometer graphene ribbons [114].

A more recent study by Chen *et al* [108] revealed the opposite effect of decreasing TC with increasing sample width for micrometer-wide graphene ribbons (GR). The authors claimed that TC increases from 205 $\text{W m}^{-1} \text{K}^{-1}$ in SLG to 2236.26 $\text{W m}^{-1} \text{K}^{-1}$ in GR with $W \sim 43\text{--}50$ μm at room temperature. Several possible reasons for such behavior have been proposed and discussed: excitation of more low-frequency phonon modes with W decrease or change in the phonon—edge localization. However, additional experimental and theoretical works are required to establish the accurate scenario. The validity of Fourier’s law for graphene was analyzed in [115]. Jo *et al* concluded [115] that linear dependence of thermal resistance on sample length, measured by Xu *et al* [107] does not reveal the violation of Fourier’s law. The authors of [115] also measured the thermal conductivity in suspended exfoliated

bi-layer graphene, using electro-thermal micro-bridge method and found TC in the range $(730\text{--}880) \pm 60$ $\text{W m}^{-1} \text{K}^{-1}$ at RT.

Another experimental study [116] employed four-wire electrical self-heating method to measure the thermal conductivity in a 169 nm wide and 846 nm long graphene ribbon. The temperature dependence of TC $\kappa \sim T^{2.79}$ was reported for temperature range 80–380 K, while $\kappa \sim T^{1.23}$ was revealed for low temperatures. The measured values of TC varied from (12.7 ± 2.95) $\text{W m}^{-1} \text{K}^{-1}$ at 80 K to (932 ± 333) $\text{W m}^{-1} \text{K}^{-1}$ at 380 K. The RT TC $\sim (349 \pm 63)$ $\text{W m}^{-1} \text{K}^{-1}$ found in this study is substantially lower than that in the large suspended graphene layers but it is in agreement with TC reported for graphene ribbons [20, 33, 107, 111, 114, 117]. The deviation of the measured data from the quasi-ballistic transport limit allowed the authors to conclude that in the considered narrow and short GNR the thermal transport is diffusive due to phonon-edge scattering.

The described experimental data confirm that graphene as superior thermal conductor is a promising material for the thermal management applications. However, production of the large high-quality graphene sheets is still a major technological challenge. The research community continues to search for inexpensive graphene-based materials with sufficiently high thermal conductivity. Recently, it was demonstrated that graphene laminate (GL) [118], reduced graphene oxide (rGO) [119] and graphene paper (Gp) [120] annealed at high temperatures possess high in-plane thermal conductivity and may be used for the thermal management as heat spreaders or fillers in the thermal interface materials. The graphene derived materials are multilayered structures of carbon layers with good in-plane interaction between atoms and weak inter-layer coupling. The RT TC varies from ~ 60 $\text{W m}^{-1} \text{K}^{-1}$ for rGO [119] to $\sim 40\text{--}90$ $\text{W m}^{-1} \text{K}^{-1}$ for GL [112] and to ~ 1400 $\text{W m}^{-1} \text{K}^{-1}$ for Gp [120]. The thermal conductivity in GL and rGO strongly depends on lattice defects and average size of grains/carbon clusters. High temperature treatment of rGO samples leads to simultaneous increase of in-plane thermal conductivity and decrease of out-of-plane thermal conductivity, resulting in exceptionally strong anisotropy of the thermal conductivity $\kappa_{\text{in-plane}}/\kappa_{\text{out-of-plane}} \sim 675$, which is by a factor of ~ 6.7 larger even than in the HOPG [119]. The theoretical dependence of the thermal conductivity on the average cluster (grain) size in GL and rGO is illustrated in figure 12.

The experimental data on the thermal conductivity of graphene and graphene-based materials are summarized in table 1. The TC values are for RT unless another temperature is indicated.

3.2. Theoretical models of thermal transport in graphene and graphene nanoribbons

The unique features of phonon transport in 2D and intensive experimental investigations stimulate theoretical studies in the graphene thermal field. The theoretical models employed for the investigation of heat conduction in graphene and GNRs can be roughly divided into two groups: Boltzmann transport equation (BTE) approach and molecular dynamics (MD)

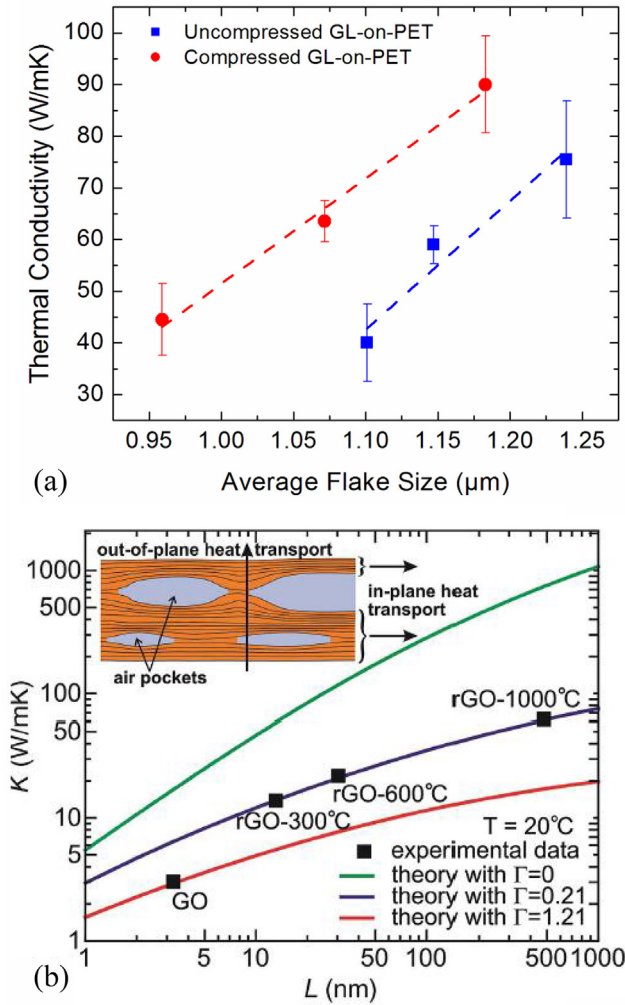


Figure 12. In-plane thermal conductivity in (a) graphene laminate and (b) reduced graphene oxide as a function of the graphene flake (domain) size. The figures are adopted from [118], copyright 2014 and [119], copyright 2015 with permissions from the American Chemical Society and John Wiley & Sons, Inc., respectively.

simulations, which include equilibrium molecular dynamics (EMD) or nonequilibrium molecular dynamics (NEMD). These models have been used in numerous theoretical studies of thermal conductivity in graphene and GNRs, which focused on the thermal conductivity dependence on flake size, defects, isotopes, strain, grain size and anharmonicity of crystal lattice.

The initial BTE-based theoretical investigations of heat conduction in graphene were carried out within the relaxation time approximation (RTA) and long-wavelength approximation (LWA) for three-phonon Umklapp scattering rates. We will refer hereafter to this approach as BTE-LWA. In his seminal works [109, 110], Klemens concluded that thermal transport in graphene sheet is 2D down to zero frequency, and, therefore, the intrinsic thermal conductivity limited by the three-phonon Umklapp scattering with the scattering rate $1/\tau_U \sim \omega^2$ demonstrates logarithmic divergence. He proposed to limit the length of the long wave-length phonons by the average size of graphene sheet L . The latter avoids the TC

divergence, resulting in the dependence of TC on the extrinsic parameter L : $\kappa \sim \log(L)$. Using simple isotropic phonon dispersion $\omega = \langle v \rangle q$, where $\langle v \rangle = 18.6 \text{ km s}^{-1}$ and average value of the Gruneisen anharmonicity parameter $\gamma = 2$, Klemens calculated the room-temperature $\kappa = 4400 \text{ W m}^{-1} \text{ K}^{-1}$ for graphene sheet with $L = 1 \text{ mm}$, which is in agreement with the first experimental findings [4, 5]. Nika *et al* [111] modified Klemens model by using a more general expression for the thermal conductivity, introducing two different average Gruneisen parameters for LA and TA branches and taking into account the difference in the phonon group velocity between them. The strong dependence of TC on L , Gruneisen parameters and temperature were predicted. It was found that the increase in L from $1 \text{ } \mu\text{m}$ to $50 \text{ } \mu\text{m}$ enhances the RT TC from 1000 to $8000 \text{ W m}^{-1} \text{ K}^{-1}$. Despite its simplicity Klemens-like BTE-LWA model describes the size dependence of TC rather accurately and in line with both experimental studies [4, 5, 106, 107] and more rigorous theoretical models developed later [26, 40, 41, 114]. Nevertheless, this model does not take into account 2D specifics of the three-phonon Umklapp scattering, which is crucial for understanding the phonon transport in graphene. More elaborate BTE-LWA calculations of the three-phonon Umklapp scattering rates, which considered all possible three-phonon transitions in graphene, allowed by the energy and momentum conservation, were reported in [26]. In this case the Umklapp scattering rate was given by:

$$\frac{1}{\tau_U^{(I),(II)}(s, \vec{q})} = \frac{\hbar \gamma_s^2(\vec{q})}{3\pi \rho v_s^2(\vec{q})} \sum_{s', s''; \vec{q}', \vec{q}''} \iint \omega_s(\vec{q}) \omega_{s'}(\vec{q}') \omega_{s''}(\vec{q}'') \times \left\{ N_0 [\omega_{s'}(\vec{q}')] \mp N_0 [\omega_{s''}(\vec{q}'')] + \frac{1}{2} \mp \frac{1}{2} \right\} \times \delta [\omega_s(\vec{q}) \pm \omega_{s'}(\vec{q}') - \omega_{s''}(\vec{q}'')] d\vec{q}' d\vec{q}'' \quad (7)$$

In equation (7) the upper signs correspond to the three-phonon processes of the first type, when a phonon with the wave vector $\vec{q}(\omega)$ absorbs another phonon from the heat flux with the wave vector $\vec{q}'(\omega')$, forming the phonon with wave vector $\vec{q}''(\omega'')$ in one of the nearest Brillouin zones; the lower signs correspond to those of the second type, when phonon $\vec{q}(\omega)$ of the heat flux decay into two phonons with the wave vectors $\vec{q}'(\omega')$ and $\vec{q}''(\omega'')$ in one of the nearest BZ. The integrals for q_{\parallel}, q_{\perp} are taken along and perpendicular to the curve segments, correspondingly, where the conditions of the energy and momentum conservation are met [26]. Using this formalism, Nika *et al* [26] found a strong dependence of the thermal conductivity on temperature, point-defects, size and edge roughness of the flake. Depending on these parameters the TC values from 2000 to $12000 \text{ W m}^{-1} \text{ K}^{-1}$ were obtained. It was also found that LA and TA phonons are the main heat carriers in graphene. The contribution from ZA phonons was small due to the large negative values of the Gruneisen parameters for the long and medium wavelength ZA phonons, resulting in their strong scattering. The latter together with the small group velocities of ZA phonons led to their smaller contribution to the phonon heat flux as compared to LA and TA phonon modes. However, equation (7) was obtained in the

Table 1. Thermal conductivity of graphene and graphene-based materials: experimental data.

κ (W m ⁻¹ K ⁻¹)	Method	Brief description	Ref.
Single-layer grapheme			
~3000–5000	Raman optothermal	Suspended; exfoliated	[4, 5]
2500	Raman optothermal	Suspended; chemical vapor deposition (CVD) grown	[95]
1500–5000	Raman optothermal	Suspended; CVD grown	[96]
600	Raman optothermal	Suspended; exfoliated; $T \sim 660$ K	[97]
2000–3800	Electrical self-heating	Exfoliated and CVD grown; $T \sim 300$ K	[98]
310 + 200/– 100 600	Electrical	Exfoliated and CVD grown; $T \sim 1000$ K Supported; exfoliated	[99]
1600–2800	Raman optothermal	Suspended; strong isotope dependence; $T \sim 380$ K	[103]
400–1800	Raman optothermal	Suspended; strong dependence on crystal lattice defects	[104]
2778.3 ± 569	Raman optothermal	Suspended, $T \sim 325$ K	[105]
Few-layer grapheme			
1300–2800	Raman optothermal	Suspended FLG; exfoliated; $n = 2-4$	[34]
50–970	Heat-spreader method	FLG, encased within SiO ₂ ; $n = 2, \dots, 21$; $T \sim 310$	[100]
560–620	Electrical self-heating	Suspended bilayer graphene; polymeric residues on the surface	[101]
302–596	Modified T-bridge	Suspended FLG; $n = 2-8$	[102]
1896 ± 390	Raman optothermal	Suspended bilayer graphene; $T \sim 325$ K	[105]
1412.8 ± 390 (730–880) ± 60	Electro-thermal micro-bridge method	Suspended twisted bilayer graphene; $T \sim 325$ K Suspended bilayer graphene; polymeric residues on the surface; 13- μ m long and 5- μ m thick	[115]
150–1200	Electrical self-heating	Suspended and supported FLG; polymeric residues on the surface	[121]
Graphene nanoribbons			
80–230	Electrical self-heating	Supported; strong size dependence	[106]
~1500	Electro-thermal micro-bridge method	Suspended, CVD grown; 9- μ m long; logarithmic dependence on the sample length	[107]
205–2236	Electrical four-wire method	TC increases with sample width decrease	[108]
1100	Electrical self-heating	Supported; exfoliated; $n < 5$	[122]
80–150	Electrical self-heating	SiO ₂ —supported; dependence on the edge roughness and defects	[123]

long wavelength approximation. Its validity for the medium and short wave-length phonons is limited. It also contains Gruneisen parameter $\gamma_s(\vec{q})$, which depends only on the anharmonic property of the phonon $\vec{q}(\omega)$, and it is averaged over the anharmonic properties of phonons $\vec{q}'(\omega')$ and $\vec{q}''(\omega'')$.

In several followed works, Lindsay *et al* [40, 41] also employed BTE approach within RTA, but without LWA for the matrix elements of three-phonon scattering. In their approach, Lindsay *et al* calculated the third-order interatomic force constants for each phonon mode and found that ZA phonons carry ~75% of heat in graphene. The three-phonon matrix elements, derived beyond the LWA, also imply the special selection rules for ZA phonons scattering: the participation of odd ZA phonons in three-phonon transitions is forbidden [40, 41]. These selection rules were not taken into account in the previous studies [26, 109–111], resulting in an overestimation of the scattering intensity for ZA phonons and underestimation of their contribution to TC. We will refer below the theoretical approach developed by Lindsay *et al* [40, 41] as BTE-IFC. It is important to note here that both BTE-LWA and BTE-IFC approaches predict strong dependence of the thermal conductivity in graphene on the extrinsic parameters: edge roughness, defects and flake size. The reported values of the thermal conductivities in these approaches are in a good agreement with each other as well as with experimental data [4, 5, 95, 96].

The first theoretical studies of thermal conductivity in graphene within MD simulations were reported in [124–126]. Using equilibrium molecular dynamics with the Brenner-type of bond order dependent potential, Che *et al* [124] studied RT thermal conductivity of carbon nanotubes (CNTs) and compared them with the calculated graphene thermal conductivity $\kappa \sim 1000$ W m⁻¹ K⁻¹. Osman and Srivastava [125] investigated thermal conductivity of CNTs and graphene using MD with the Tersoff–Brenner potential for C–C interaction. The RT TC of graphene $\kappa \sim 1500$ W m⁻¹ K⁻¹ was obtained in their calculations. One should note that in most of the MD calculations the absolute values of TC are limited by the size of the simulated sample. Berber *et al* [126] reported on higher value of RT TC in graphene $\kappa \sim 6600$ W m⁻¹ K⁻¹ withing combined equilibrium and nonequilibrium MD with Tersoff interatomic potential. The thermal transport in GNRs was considered in [127–129] in the framework of EMD and NEMD with Brenner [127], Tersoff [128] and Stillinger–Weber [129] type potentials. It was established that in few-nanometer size GNRs, the thermal conductivity depends on edge chirality and defects of crystal lattice [127]. Zigzag edge GNRs (ZGNRs) demonstrated higher thermal conductivity than arm-chair edge GNRs (AGNRs), while defects suppressed thermal conductivity twice [127] from $\kappa \sim 1400$ W m⁻¹ K⁻¹ to 700 W m⁻¹ K⁻¹ at RT. The length and strain dependence of TC in 20-AGNR

and 10-ZGNR was investigated in [128]. In the considered range of the length from 10 nm to 60 nm, the TC increased with L as $\kappa \sim L^n$, where $n = 0.47$ for 20-AGNR and $n = 0.35$ for 10-ZGNR [129]. The 15%—strain decreased TC by a factor of ~ 4.5 for 10-ZGNR and by a factor of ~ 2 for 20-AGNR. The strong thermal rectification effect in GNRs with different shapes was also elucidated [127, 129]. Readers interested in more detailed description of theoretical results on thermal transport in graphene and GNRs, reported between 2009 and 2012 are referred to different reviews [6, 20–24]. Below we focus on the review of more recent theoretical results, their discussion and comparison with earlier findings.

The thermal transport in bicrystalline GNRs with different symmetric tilt grain boundaries was investigated in [130] using both NEMD and BTE. Authors demonstrated that thermal conductivity is determined by phonon scattering on edge roughness and grain boundaries. The strong length and temperature dependence of TC was also revealed. The RT thermal conductivity $\sim 4000 \text{ W m}^{-1} \text{ K}^{-1}$ was found for SLG sheet with $10 \mu\text{m}$ length. The substantially lower values of RT TC ~ 168 and $277 \text{ W m}^{-1} \text{ K}^{-1}$ were predicted for pristine and bicrystalline GNRs with the width of 4.1 nm due to the strong phonon scattering on edges and grain boundaries.

Shen *et al* [131] carried out theoretical investigation of thermal transport in GNRs, using BTE-RTA and Klemens-like formula [109, 110] for three-phonon Umklapp scattering. The dependence of phonon frequencies on q was considered as linear for in-plane acoustic phonons and quadratic for out-of-plane acoustic phonons over entire BZ. To take into account the selection rules for ZA phonons scattering [40–42] authors of [131] increased their relaxation time by a factor of 3 because of only 4 types of three-phonon processes from 12 are allowed: $\text{ZA} + \text{ZA} \leftrightarrow \text{LA}$, $\text{ZA} + \text{ZA} \leftrightarrow \text{TA}$, $\text{LA} + \text{ZA} \leftrightarrow \text{ZA}$ and $\text{TA} + \text{ZA} \leftrightarrow \text{ZA}$. The obtained results show that thermal conductivity of GNRs strongly depends on edge roughness, flake length and temperature, which is in a good agreement with the previous theoretical studies [26, 33, 40, 41, 111, 114]. The RT TC of $1 \mu\text{m}$ wide and $10 \mu\text{m}$ long GNR decreases from $\sim 4700 \text{ W m}^{-1} \text{ K}^{-1}$ to $\sim 2750 \text{ W m}^{-1} \text{ K}^{-1}$ with the change of phonon-edge scattering from purely specular ($p = 1$) to purely diffusive ($p = 0$). This decrease in TC value is weaker in comparison with that reported by Nika *et al* [114]. The difference can be attributed to different formulas of Umklapp scattering rates used: in [114] the Umklapp scattering rates were calculated beyond Klemens-like formula, taking into account all possible 2D three-phonon processes allowed by the momentum and conservation laws.

Another theoretical study of the thermal conductivity of suspended and supported GNRs employed continuum approach for the phonon energy spectra calculations, Callaway formalism for thermal conductivity calculations and standard formulas for Normal, Umklapp, point-defects and rough-edge phonon scatterings [132]. Authors found that for narrow GNRs with width $< 50 \text{ nm}$ in the energy spectra of acoustic phonons appear many confined branches, resulting in dependence of the average phonon group velocities on the phonon energy. The average velocities in GNRs are close to those in SLG only at small energies $\hbar\omega < \sim 10 \text{ meV}$ and smaller than that in SLG

for wide energy range 10–180 meV [132]. Another important observation of this study was strong-enough dependence of TC on extrinsic parameters of GNRs: point defects, edge quality and sample size. These findings are in line with many previous theoretical and experimental results [6, 20, 21, 26, 33, 40, 41, 106, 107, 111, 114]. The dependence of the thermal conductivity on temperature for 260 nm-long and 45 nm-wide supported GNR, calculated in [132] is in agreement with the TC values measured for GNR with the same size in [106]. It is also important to note here that the decreasing of phonon group velocity in GNRs due to phonon confinement found in [132] is in qualitative agreement with the theoretical predictions made earlier for semiconductor thin films and nanowires [133–136].

The strain effect on the thermal transport in graphene was theoretically investigated by Lindsay *et al* [43] using the Boltzmann–Peierls equation. The authors employed the density functional perturbation theory (DFPT) for calculating the harmonic interatomic force constants required for accurate description of the phonon scattering rates. The results revealed strong dependence of TC on temperature and sample size, and relative weak dependence of TC on weak isotropic tensile strain ($\sim 1\%$). These findings are in line with the previous study [137]. At the same time, stronger dependence of TC on small tensile strain in graphene was predicted in [53], using continuum approach for phonons and BTE-LWA. The discrepancy may be attributed to difference in the phonon dispersion and phonon scattering rates. The latter confirms that accurate description of phonons in graphene materials is required for capturing main features of thermal conductivity. This assessment coincides with the conclusions made by Fugallo *et al* [138], which reported on the thermal transport of collective phonon excitations in graphene. According to Fugallo *et al* [138], BTE-RTA approach strongly underestimates the TC in graphene and overestimates the influence of the strain. In contrast, the thermal conductivities calculated from the exact solution of BTE without single mode RTA, resulting in collective phonon excitations, were in a good agreement with the experimental data. Fugallo *et al* [138] also found the strong dependence of TC on the graphene flake length. The high value of RT TC $\sim 3500 \text{ W m}^{-1} \text{ K}^{-1}$ which is close to the experimental values [4, 5] was obtained for very long flake ($L \sim 1 \text{ mm}$).

Many recent theoretical results on thermal transport in graphene were obtained using MD simulations [139–146]. Chen and Kumar [139] investigated thermal transport in graphene supported on copper within equilibrium MD simulations and relaxation time approximation. The interaction with Cu substrate was modeled using the Lennard–Jones potential. The authors found that coupling to substrate significantly influences low-energy and low-wave vector part of phonon energy dispersions in supported SLG as compared with suspended SLG. The RT TC decreases with increasing the interaction strength between carbon and copper atoms from $\sim 1800 \text{ W m}^{-1} \text{ K}^{-1}$ (suspended SLG) to $1000 \text{ W m}^{-1} \text{ K}^{-1}$ (supported SLG with strong coupling to substrate). The effect of strain and isotopic disorder on thermal transport in suspended SLG were studied by Pereira and Donadio [140] using equilibrium

MD simulations. The authors predicted that the thermal conductivity of unstrained SLG is finite and converges with the sample size at finite temperature. However, TC of the strained graphene diverges logarithmically with the sample size when strain exceeds a threshold value of 2%. The authors concluded that ZA modes are important for obtaining the finite TC in suspended SLG because they provide the essential scattering channels to limit the thermal conductivity. In unstrained graphene, the population of ZA modes reduces, while their lifetime increases, resulting in divergence of TC. The authors also shown that isotopic effect strongly influences the thermal conductivity: RT TC decreases from $\sim 1000 \text{ W m}^{-1} \text{ K}^{-1}$ to $\sim 450 \text{ W m}^{-1} \text{ K}^{-1}$ with increasing of ^{13}C concentration from 0 (pure ^{12}C graphene) to 50%. This result is in a good agreement with experimental measurements [103].

Other MD studies [141–146] confirmed that structural defects of the crystal lattice may significantly suppress the thermal conductivity in graphene and change the temperature dependence of TC. Khosravian *et al* [141] found that RT TC of graphene flake decreases from $180 \text{ W m}^{-1} \text{ K}^{-1}$ to $80 \text{ W m}^{-1} \text{ K}^{-1}$ with increasing the number of multi-vacancy defects. Fthenakis *et al* [142] demonstrated that TC depends sensitively on whether the defects are isolated, form lines or form extended arrangements in haeckelites. The presence of nonhexagonal rings in crystal lattice made the thermal conductivity anisotropic [142]. According to Fthenakis *et al* [142], the TC in graphene with defects can be suppressed up to two orders of magnitude depending on temperature and defects type. Yang *et al* [146] considered thermal transport in 21.2 nm long and 3.8 nm wide AGNRs with triangular vacancy (TV) defect and concluded that increase of TV size leads to the suppression of thermal conductivity. It was found that presence of TV defect with 25 removed carbon atoms decreases the RT TC by more than 40% from $230 \text{ W m}^{-1} \text{ K}^{-1}$ to $150 \text{ W m}^{-1} \text{ K}^{-1}$ due to phonon-defect scattering.

The thermal conductivity in nitrogen-doped graphene and GNRs was studied in [143, 145] within reverse NEMD [143] and EMD based on Green–Kubo method [145]. Yang *et al* [143] found that thermal conductivity of N-doped GNRs is smaller than that in GNRs without doping and strongly depends on nitrogen atoms distribution. The RT TC $\sim 50 \text{ W m}^{-1} \text{ K}^{-1}$ was found for 11 nm—long and 2 nm—wide GNR with rhombus shape doping, which is by a factor of ~ 1.9 smaller than that in GNR without doping [143]. Goharshadi and Mahdizadeh [145] reported on 59.2% decrease of RT TC in nitrogen-doped graphene with low concentration of $N \sim 1\%$.

Feng *et al* [144] carried out theoretical study of the phonon relaxation time, phonon mean-free path and thermal conductivity in defected graphene within the normal mode analysis based on equilibrium MD. Four types of defects were considered: isotopes, Stone–Thrower–Wales (STW) defects, mono vacancies (MV) and double vacancies (DV). The authors have shown that the thermal conductivity strongly decreases in defected graphene: 1.1% of STW (MV) defects suppresses the thermal conductivity by $\sim 90\%$ (95%). These findings are in a general accordance with earlier MD simulations [147–149]. The analysis of the frequency dependence of the phonon relaxation time

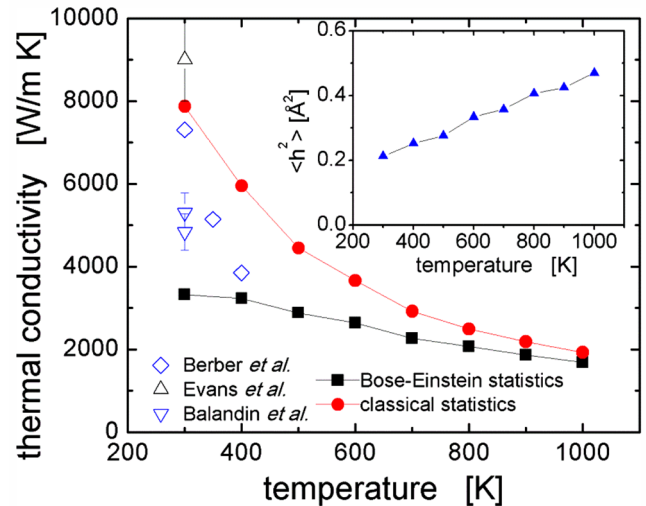


Figure 13. Thermal conductivity of suspended single-layer graphene as a function of temperature calculated for the phonon number obeying the Bose–Einstein and classical statistics. The insert shows the temperature dependent out-of-plane displacement. The data points from [4, 126, 160] are shown by diamonds and triangles. The figure is reproduced from [150], copyright 2014 with the permission from the American Institute of Physics.

for point-defect scattering revealed deviation from traditionally used dependence: $\tau_{p-d} \sim \omega^4$ for 2D materials and $\tau_{p-d} \sim \omega^3$ for 2D materials. According to Feng *et al* [144], $\tau_{p-d} \sim \omega^n$, where n depends on the type of defects: $n = 1$ for STW defects and $n = 1.1–1.3$ for MV and DV defects, with exception of a few long-wavelength phonons, demonstrating $\sim \omega^4$ dependence. The data scatter in the thermal conductivity values in graphene with defects shows that additional investigations are required, because both thermal conductivities and predicted $\tau_{p-d}(\omega)$ dependence may be strongly affected by the simulation domain size, used in the MD calculations. Wei *et al* [150] studied phonon thermal transport in SLG, using spectra-based MD simulations and Tersoff potential for carbon–carbon interaction. Depending on the temperature, TC values in the range $2000–8000 \text{ W m}^{-1} \text{ K}^{-1}$ for classical statistics (CS) and $2000–3500 \text{ W m}^{-1} \text{ K}^{-1}$ for Bose–Einstein statistics (BES) were obtained (see figure 13). The difference between TC values calculated using BES and CS is large enough at RT and decreases with temperature. Thus, different phonon statistics employed in different MD models may lead to large discrepancy in TC values near RT. The ballistic thermal conductance in GNRs was investigated in [151] in the presence of single atom vacancies (SAV). It has been demonstrated that central localized SAV affects thermal transport of the out-of-plane phonon modes while supported GNRs edges reduce thermal transport of the in-plane phonons. As a result, a drop in the thermal conductance of the supported-edge GNRs with SAV was predicted in a comparison with free-standing GNRs without SAV [151].

The electron contribution to heat conduction in graphene has not been studied in details. The first estimates from the experimental data using the Wiedemann–Franz law revealed negligible contribution of electrons to the thermal transport as compared to phonons [4]. Recent calculations within the density functional

Table 2. Thermal conductivity in graphene and graphene nanoribbons: theoretical models.

κ (W m ⁻¹ K ⁻¹)	Method	Brief description	Ref.
Single-layer grapheme			
2000–8000	BTE-LWA + all possible three-phonon transitions	TC dependence on edge roughness, flake width and Gruneisen parameter	[26]
1500–3500	BTE-IFC	TC dependence on flake size	[40]
~3100	BTE-IFC + density function perturbation theory	$L = 10 \mu\text{m}$; TC dependence on flake size; weak dependence of TC on small isotopic strain (<1%)	[43]
2000–4000	BTE-LWA + continuum approach	Strong isotope, point-defects and strain influence	[52, 53]
4400	BTE-LWA	Average $\gamma = 2$ and average $\langle v \rangle = 18.6 \text{ km s}^{-1}$ for in-plane phonons; strong size dependence $\kappa \sim \log(L)$	[109, 110]
1000–8000	BTE-LWA	Different average γ and different group velocities for in-plane phonons; strong size dependence $\kappa \sim \log(L)$	[111]
100–8000	BTE-IFC	TC dependence on flake size, shape and edge roughness	[114]
1000	EMD	Brenner-type bond order interatomic potential (IP)	[124]
~1500	MD	Tersoff–Brenner potential for C–C IP	[125]
~6600	EMD and NEMD	Tersoff IP	[126]
4000–6000	BTE-LWA	Strong dependence on the strain larger than 4%	[137]
~3500	BTE beyond RTA; collective phonon excitations	Flake length $\sim 1 \text{ nm}$; strong length dependence; weak Dependence on strain and weak dependence on length in strained graphene	[138]
1800	EMD	6 nm \times 6 nm sheet; isolated	[139]
1000–1300	EMD	6 nm \times 6 nm sheet; Cu—supported; strong dependence on the interaction strength between graphene and substrate	
~1000	EMD	Strong isotopic effect	[140]
300–500	NEMD	Strong defect influence	[142]
400–2400	BTE-LWA	Strong dependence on defect density and edge roughness	[104]
800–1250	NEMD	Strong dependence on defect density	
2900	NEMD	Strong dependence on the vacancy concentration	[147]
~3300	Spectra-based MD + Tersoff IP	Bose–Einstein statistics	[150]
~8000		Classical statistics	
~2430	BTE-IFC	$\kappa(\text{graphene}) \geq \kappa(\text{carbon nanotube})$	[153]
4000	ballistic	Strong width dependence	[154]
20000	VFF + ballistic regime	Flake length $\sim 5 \mu\text{m}$; strong width and length dependence	[155]
100–550	NEMD	Flake length $L < 200 \text{ nm}$; strong length and defect dependence	[156]
3000	NEMD	Flake length $\sim 15 \mu\text{m}$; strong size dependence	[157]
2360	NEMD	$L \sim 5 \mu\text{m}$; strong length dependence	[158]
100–600	Non-equilibrium Green functions	Strong dependence on grain size and line defects	[159]
~256	EMD and NEMD	TC in SiO ₂ —supported SLG is by an order of magnitude lower than in suspended SLG	[160]
Electronic TC ~ 300	Density functional theory + many-body perturbation theory	Strong dependence on the impurity	[152]
Few-layer grapheme			
1000–4000	BTE-LWA, $\gamma_s(q)$	$n = 8-1$, strong size dependence	[34]
1000–3500	BTE-IFC	$n = 5-1$, strong size dependence	[41]
2000–3300	BTE-IFC	$n = 4-1$	[42]
580–880	NEMD	$n = 5-1$, strong dependence on the Van-der Waals bond strength	[164]
Graphene nanoribbons			
5500	BTE-LWA	GNR with width of $5 \mu\text{m}$; strong dependence on the edge roughness	[33]
400–600	NEMD	$K \sim L^{0.24}$; $100 \text{ nm} \leq L \leq 650 \text{ nm}$	[117]
2000	MD + Brenner IP	$T = 400 \text{ K}$; $1.5 \text{ nm} \times 5.7 \text{ nm}$ zigzag GNR; strong edge chirality influence	[127]
200–900	NEMD + Tersoff IP	Strong strain and length dependence $\kappa \sim L^n$, where $n = 0.47$ for 20-AGNR and $n = 0.35$ for 10-ZGNR; $L = 10 \text{ nm}-60 \text{ nm}$	[128]
168–4000	BTE-LWA, NEMD	Bicrystalline GNRs; $4.1 \text{ nm} \leq L \leq 10 \mu\text{m}$ TC dependence on length	[130]
2750–4000	BTE-LWA	GNRs with $L = 10 \mu\text{m}$ and $W = 1 \mu\text{m}$; dependence on edge roughness	[131]

(Continued)

Table 2. (Continued)

κ ($\text{W m}^{-1} \text{K}^{-1}$)	Method	Brief description	Ref.
60–70	BTE-LWA	Narrow GNRs with $W < 50$ nm; confined phonon branches; strong edge scattering	[132]
~50	Reverse NEMD	Nitrogen-doped 11 nm—long and 2 nm—wide GNRs; strong dependence on nitrogen atoms distribution	[143]
~2500	EMD + Tersoff IP	Nitrogen-doped 10 nm—long and 2 nm—wide GNRs; strong dependence on nitrogen concentration	[145]
~230	Reverse NEMD	21.2 nm—long and 3.8 nm—wide AGNRs; strong dependence on triangular vacancy size	[146]
1000–7000	EMD + Tersoff IP	Strong ribbon width and edge dependence	[160]
30–80	Reverse NEMD + AIREBO IP	10—zigzag and 19—arm-chair nanoribbons; strong defect dependence	[161, 162]
3200–5200	EMD	Strong GNRs width (W) and length dependence; $9 \text{ nm} \leq L \leq 27 \text{ nm}$ and $4 \text{ nm} \leq W \leq 18 \text{ nm}$	[163]
100–1000	BTE-LWA	SiO_2 —supported GNRs; strong edge and width dependence	[166]
500–300	NEMD	Few-layer G10-ZGNR, $n = 1, \dots, 5$	[167]
Graphene laminate			
35–90	BTE-LWA	GL is modeled as a multilayer film composed of graphene flakes with different average size; strong dependence on defects and average size of graphene flakes	[118]
Reduced graphene oxide			
1.5–1000	BTE-LWA	rGO is modeled as multilayer graphene film with crystal lattice defects; strong dependence on defects and average length of graphene clusters	[119]

theory and many-body perturbation theory demonstrated higher values of the electronic thermal conductivity κ_{el} at RT [152]; $\kappa_{\text{el}} \sim 300 \text{ W m}^{-1} \text{K}^{-1}$, which constitutes around 10% of the total TC. It was also found that electronic TC strongly decreases with the rise of impurity concentration [152]. One should note that strong electrostatic bias of graphene resulting in high concentration of electrons can change the relative contribution of electrons to heat conduction. The theoretical data on thermal conductivity in graphene and GNRs are presented in table 2 for RT (unless another temperature is indicated). As it follows from table 2, the thermal conductivity of graphene materials with small concentration of lattice defects is determined not only by the lattice anharmonicity (as it is usually the case for bulk crystalline materials) but also by the flake size and shape. Introduction of different types of crystal lattice defects, e.g. vacancies, isotopes and impurities, leads to a dramatic reduction of the thermal conductivity. Majority of the theoretical results obtained both in BTE and MD approaches are in a qualitative agreement with experimental results summarized in table 1, including in the aspects of the size, temperature and lattice defects dependence. Relatively large differences in the predicted theoretical values of RT thermal conductivity in graphene materials may be attributed to (i) the interatomic potentials used; (ii) differences in the simulation domain size in MD approaches; (iii) different formulation of the heat auto-correlation functions; and (iv) specifics of the frequency dependences of the Umklapp and point-defect phonon scattering rates.

3.3. Contribution of different phonon branches to thermal conductivity

The relative contribution of different phonon polarization branches to thermal conductivity in graphene is one of the

most interesting questions related to the physics of thermal transport in 2D crystal lattices. A number of theoretical studies [26, 33, 40–43, 109–111, 131, 132, 139, 144, 150, 166, 168, 169] investigated the polarization branch-dependent thermal conductivity in graphene and GNRs within both BTE approach and MD approaches. Klemens [109, 110] assumed that ZA modes carry negligible amount of heat owing their small group velocities and large Gruneisen parameter. The calculations of TC, employing BTE-LWA approach [26], confirmed Klemens' assumption: the contribution of ZA modes to TC was smaller than 1% due to both small group velocities and large values of $|\gamma_{\text{ZA}}(q)|$ for long and medium wavelength ZA phonons. However, calculations of TC within BTE-IFC approach predicted dominant role of ZA modes in thermal transport [40–42]. Lindsay *et al* [40] found that the contribution of ZA phonons to RT TC in SLG constitutes 75% for 10 μm -long graphene flake and decreases down to 40% in FLG with number of layers $n > 4$ [41]. The breaking of SLG selection rules for ZA phonons scattering in FLG was indicated as the primary reason for smaller contribution of ZA phonons to TC [41]. Singh *et al* [42] also employed BTE-IFC approach for the investigation of thermal transport in SLG and FLG. Their results [42] were in a good agreement with those obtained by Lindsay *et al* [40, 41]. At the same time, more recent studies of thermal conductivity in graphene and GNRs reported various values for the relative contributions of ZA modes to TC: from several to 40%. Moreover, strong dependence of ZA modes contribution to TC on temperature, sample size and defects was revealed.

Liu *et al* [130] demonstrated that relative contribution of different phonon branches to TC for bicrystalline GNRs depends on the temperature: at low temperatures ZA modes

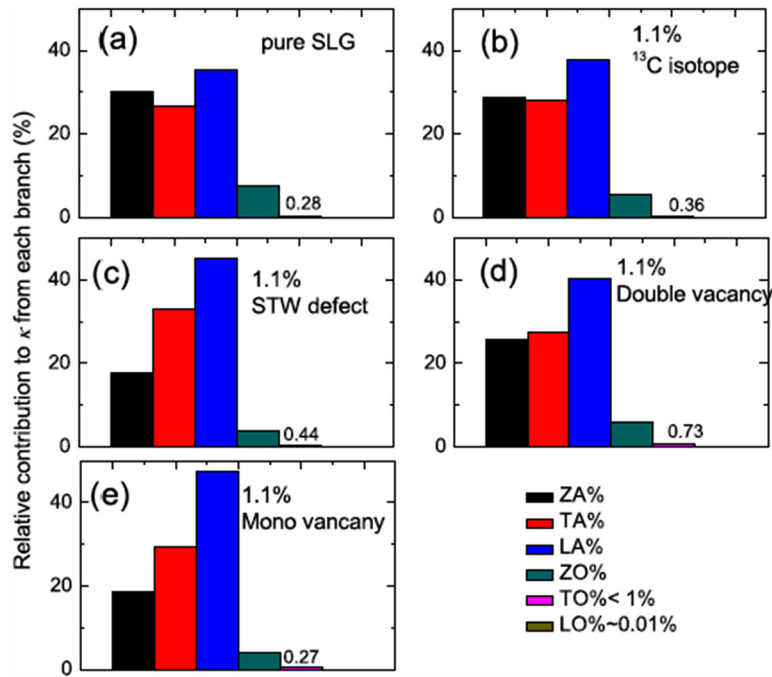


Figure 14. Relative contribution of the phonon branches to the thermal conductivity of graphene calculated using EMD: pure SLG (a), SLG with ^{13}C isotopes (b) and SLG with STW (c), double vacancy (d) and mono vacancy (e) defects. Note that various theoretical approaches give a wide range of relative contributions depending on the assumptions used. External factors such as presence or absence of a substrate and nature of the defects also affect the relative contributions. The figure is reproduced from [43], copyright 2014 with the permission from the American Physical Society.

dominate the thermal transport, while the contribution of LA and TA modes becomes more important for $T > 150\text{ K}$. Bae *et al* [106] calculated the contribution of different phonon branches to TC in GNRs within the BTE approach. For all considered GNRs, the contribution of ZA phonons to TC was smaller than that of LA or TA modes. The authors also concluded that large intrinsic MFP of LA and TA modes makes them more sensitive to GNR edge disorder while ZA modes are predominantly affected by substrate scattering [106].

Shen *et al* [131] found that the contribution of ZA phonons to TC of GNRs varies strongly with temperature and sample size. In $1\ \mu\text{m}$ -wide and $10\text{-}\mu\text{m}$ long GNR, the contribution of the out-of-plane phonons decreases fast with increasing temperature: from 80% at $\sim 10\text{ K}$ to 20% at 80 K. At temperature $T > 100\text{ K}$, the in-plane phonons carry 90% of heat. The contribution of the in-plane phonons to thermal conductivity also increases with increasing ribbon length. For $100\text{-}\mu\text{m}$ long GNR, the contribution of TA, LA and ZA phonons to RT TC is ~ 5000 , ~ 3000 and $\sim 500\text{ W m}^{-1}\text{ K}^{-1}$, correspondingly. Thus, in large graphene flakes, the ZA phonons carry less than 5% of heat.

Nissimagoudar and Sankeshwar [132] also concluded that the contribution of different phonon branches to TC of GNRs strongly depends on temperature: ZA modes are the main heat carries for low temperatures $T \leq T_{\text{lim}}$, while LA and TA phonons dominate thermal transport for $T > T_{\text{lim}}$. The value of T_{lim} depends on the GNR size and is different for suspended and supported GNRs. For $1\ \mu\text{m}$ -long and 5 nm -thick GNRs T_{lim} is $\sim 250\text{ K}$ for suspended GNRs and $\sim 150\text{ K}$ for supported GNRs [132]. The deviation from the quadratic phonon dispersion $\omega \sim q^2$ of ZA branch in graphene [38], resulting in lower

values of group velocities, could slightly decrease the relative contribution from ZA phonons to TC [131, 132].

MD simulations were also intensively employed for investigating the relative importance of each phonon polarization branch to thermal transport [139, 144, 150, 160, 168, 169]. Ong and Pop concluded [165] that coupling to the substrate reduces the thermal conductivity of SiO_2 -supported graphene by an order of magnitude in comparison with suspended SLG due to the damping of the ZA phonons [165]. This conclusion is in line with findings from [41, 42]. However much smaller contribution from ZA phonons to TC was reported in [139, 144, 150]. Chen and Kumar [139] predicted that LA, TA and ZA phonons carry $\sim 40\%$, 20% and 22% of total heat, respectively in suspended SLG at RT. The contribution of optical phonons was found as large as $\sim 18\%$. It was established that in supported SLG the contribution to RT TC changes and constitutes $\sim 50\%$ for LA phonons, $\sim 21\%$ for TA phonons, $\sim 7\%$ for ZA phonons and $\sim 22\%$ for optic phonons.

Wei *et al* [150] employed the spectral-based MD simulations for analysis of the contribution of different phonon modes to thermal conductivity. It was found that coupling to a substrate reduces the contribution of ZA phonons from 41.1% in suspended SLG to $\sim 20\%$ in supported SLG [150]. Feng *et al* [144] investigated the branch-dependent thermal conductivity in defected graphene, using the normal mode analysis based on the equilibrium MD. It was concluded that in pristine SLG, the LA/TA/ZA phonons carry $\sim 35\%$ / $\sim 27\%$ / $\sim 30\%$ of heat, while the contribution from ZO phonons is about 7% [144]. In STW-defected and MV-defected graphene the contribution of ZA modes reduces to 20%, while contribution from LA modes increases to 50%. The decrease of the contribution of

Table 3. Contribution of different phonon polarization branches to thermal conductivity in graphene and GNRs.

	Model	Description	Ref.
SLG	BTE-LWA	Assumption that only LA and TA phonons participate in thermal transport (TT)	[109–111]
SLG	BTE-LWA	LA + TA ~ 99%	[26]
SLG	BTE-IFC	ZA ~ 75%; TA ~ 15%; LA ~ 9%	[40]
FLG	BTE-IFC	ZA contribution decreases from ~75% for SLG to 38% for 6-layer FLG; TA and LA contribution is insensitive to number of layers n : TA ~ 15% and LA ~ 9%	[41]
FLG	BTE-IFC	ZA phonons are dominate heat carries; thermal conductivity decreases with rise of n owing decrease of ZA phonon contribution	[42]
SLG	BTE-LWA	Strong dependence of ZA contribution on the temperature; ZA phonons are the main heat carriers for $T < 50$ K, while for $T > 200$ K in-plane acoustic phonons dominate TT; at RT TA/LA/ZA contribution is ~65%/25%/10%	[33]
SiO ₂ —supported GNRs	BTE-LWA	Strong dependence of ZA contribution on the temperature; ZA phonons dominate thermal transport for $T < 100$ K, while for $T > 200$ K TA and LA phonons are the main heat carriers	[166]
SLG	BTE-IFC	Flake length $L = 10 \mu\text{m}$; ZA ~ 76%, LA + TA ~ 20%	[43]
GNRs	BTE	ZA contribution is smaller than TA or LA contribution	[106]
GNRs	BTE-LWA	Strong temperature and flake size dependence; ZA contribution < ~5% for large flakes	[131]
GNRs	BTE-LWA	Strong dependence of ZA contribution on the temperature and flake size; ZA modes dominate TT at low temperatures, while TA and LA modes are dominant heat carriers for medium and high T	[132]
Suspended and SiO ₂ -supported graphene	EMD and NEMD	ZA phonons dominate TT	[165]
SLG	EMD	LA ~ 40%, TA ~ 20%, ZA ~ 22%, optic phonons ~ 18% in suspended SLG; LA ~ 50%, TA ~ 21%, ZA ~ 7%, optic phonons ~ 22% in supported SLG	[139]
SLG	Spectral-based MD	ZA ~ 41.8% in suspended SLG and ~20% in supported SLG	[150]
SLG	EMD	LA ~ 35%, TA ~ 27%, ZA ~ 30%, ZO ~ 7% in pristine SLG; LA ~ 50%, ZA ~ 20% in SLG with defects	[144]
SLG	EMD + time – domain TC	Collective phonon excitations; ZA contribution ~78%	[168, 169]

ZA modes in defected graphene was explained by the breakdown of reflection symmetry in the direction perpendicular to graphene layer [144]. At the same time, Gill-Comeau and Levis [168, 169], considering the collective phonon excitations in graphene, concluded that ZA phonons dominate the thermal transport, carrying ~78% of heat. Figure 14 illustrates how sensitive the relative contribution of each phonon polarization branch can be to the amount and nature of the defects in graphene.

From the review of these theoretical and computational results we can conclude that the studies, employing BTE-LWA approach, usually, predict small contribution from ZA phonons to RT TC due to their small group velocities and overestimation of their scattering. The overestimation comes from two reasons: (1) omission of ZA selection rules and (2) large values of $|\gamma_{ZA}(q)|$ for long- and medium wavelength phonons $\gamma_{ZA}^2(q) \gg \gamma_{LA}^2(q), \gamma_{TA}^2(q)$ [57], resulting in shorter life-time

for ZA phonons $\tau_U(q) \sim 1/\gamma^2(q)$. In contrast, BTE-IFC studies predict the dominant role of ZA phonons in thermal transport in suspended graphene owing their weaker scattering as compared with LA and TA modes. Weak scattering of ZA phonons is explained both by the ZA selection rule, which limits scattering, and small values of 3rd order IFCs for a certain modes. The high—order unharmonic processes, which are not taken into consideration in BTE-LWA and BTE-IFC, could significantly change the relative branch contribution. The latter is confirmed by several independent MD studies, predicting larger contribution to TC from the in-plane acoustic phonons [139, 144, 150]. However, other MD studies demonstrated opposite view [165, 168, 169]. Including collective excitations in the thermal transport models significantly change the final conclusions [138, 168, 169]. The discrepancy in reviewed results suggests that additional theoretical and experimental

studies are required to shed light on relative contributions from different branches to thermal conductivity of graphene materials. In table 3 we summarize the branch-dependent contributions to thermal conductivity reported up to date. The data are presented for the room temperature unless different temperature is indicated.

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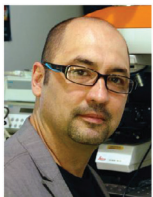
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