Phononics of Graphene and Graphene Composites

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Spins and Heat In Nanoscale Electronic Systems

The Brillouin Medal Lecture Arizona, June 2019



Outline

Introduction and Motivations

- Graphene
- Phonons
- Thermal conductivity
- Thermal Conductivity of Graphene
 - Raman spectroscopy
 - Optothermal technique
 - Theoretical interpretation
- Composites with Graphene
 - Thermal interface materials
 - Thermal phase change materials
 - Electromagnetic shielding
- Outlook







Graphene's applications we hoped for touch screens and other electronics





Flexible graphene sheet with silver electrodes printed on it can be used as a touch screen when connected to control software. Credit: Byung Hee Hong, SKKU.

http://www.technologyreview.com/computing/25633/page1/





Graphene's applications we are still hoping and working for: transistors, sensors, interconnects, voltage controlled resistors











nature nanotechnology

LETTERS PUBLISHED ONLINE: 4 JULY 2016 | DOI: 10.1038/NNANO.2016.108

A charge-density-wave oscillator based on an integrated tantalum disulfide-boron nitridegraphene device operating at room temperature

Guanxiong Liu¹, Bishwajit Debnath², Timothy R. Pope³, Tina T. Salguero³, Roger K. Lake² and Alexander A. Balandin^{1*}



Jackets, rackets, hair dye and satellites: How graphene is changing the global

Commercial graphene applications we got so far...

economy

CIENCE & TECH NOV 21 2018 VICTORIA ZAVYALOVA



All 1,000 graphene enhanced jackets were sold out in less than three days for the price of \$695 per item.





Graphene forms a gentle film around each and every hair strand. The color lasts for at least 30 washes, just like any conventional chemicalbased dye. The graphene-enhanced hair is also anti-static and antibacterial so the hair will stay clean longer. 5



Part I: Thermal Properties of Graphene – Fundamental Science

mature

REVIEW ARTICLE PUBLISHED ONLINE: 22 JULY 2011 | DOI: 10.1038/NMAT3064

Thermal properties of graphene and nanostructured carbon materials

Alexander A. Balandin

IOP Publishing Rep. Prog. Phys. 80 (2017) 036502 (21pp)

Reports on Progress in Physics doi:10.1088/1361-6633/80/3/036502 OCTOBER 2009 · IEEE SPECTRUM · INT 29

Review

Phonons and thermal transport in graphene and graphene-based materials

https://balandingroup.ucr.edu/index.html

Denis L Nika^{1,2} and Alexander A Balandin¹



Basics of Thermal Conductivity

Definitions and Basic Theory

Fourier's law:

$$\frac{\dot{Q}}{S} = -K\nabla T$$

Phonon vs. electron conduction:

$$\frac{K_e}{\sigma} = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 T$$

Heat current carried by phonons :

$$Q = \sum_{q,j} N_{\mathbf{q},i}(\mathbf{q}) \hbar \omega_i(\mathbf{q}) \frac{\partial \omega}{\partial \mathbf{q}},$$

RT thermal conductivity of important materials: Silicon (Si): 145 W/mK SiO₂: 0.5 – 1.4 W/mK Copper: 385 - 400 W/mK RT thermal conductivity for carbon materials: Diamond: 1000 – 2200 W/mK Graphite: 20 – 2000 W/mK (orientation) DIC: 0.1 - 10 W/mKCNT: ~3000 - 3500 W/mK

CNT: ~1758 – 5800 W/mK

According to J. Hone, M. Whitney, C. Piskoti, A. Zettl, A. Phys. Rev. B 1999, R2514 (1999)



Thermal Conductivity of Bulk Carbon Materials



← Bulk graphite: 2000 W/mK at RT

← Order of magnitude difference in high-quality graphite depending on the method and polycrystallinity

A.A. Balandin, "Thermal properties of graphene and nanostructured carbon materials," Nature Materials, 10, 569 - 581 (2011).

What happens with thermal conductivity of 3D crystal if we thin it down to 2D crystal?



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Thermal Conductivity at Nanoscale: Extrinsic Phonon Transport Regime

Thermal conductivity usually decreases as one goes from bulk material to nanostructure or thin film



←Thermal conductivity of bulk Si at room temperature: K= 148 W/m-K

← Thermal conductivity of Si nanowire with cross section of 20 nm x 20 nm: K=13 W/mK

 \rightarrow Phonon thermal conductivity:

$$K_p = (1/3)C_p \upsilon \Lambda$$

→ Boundary-limited MFP ($\Lambda = v\tau$):

$$\frac{1}{\tau_B} = \frac{\upsilon}{D} \frac{1-p}{1+p}$$

$$K_p \sim C_p \upsilon \Lambda \sim C_p \upsilon^2 \tau_B \sim C_p \upsilon D$$



Thermal Conductivity of 2D Crystals in Intrinsic Phonon Transport Regime: Infinity



- → The momentum conservation in 1D and 2D systems with anharmonicity leads to the divergence of the intrinsic thermal conductivity K with the system size
- → Thermal conductivity remains finite and does not depend on the system size in 3D



Divergence of the Lattice Thermal Conductivity in 2D and 1D Crystal Lattices

The intrinsic thermal conductivity of 2-D or 1-D anharmonic crystals is anomalous.



Data is after S. Lepri et al. Phys. Rep., 377, 1 (2003).

K ~ log(N) in 2D K ~ N^α in 1D, $\alpha \neq 1$ N – system size

K. Saito, et al., *Phys. Rev. Lett.* (2010).
 A. Dhar. *Advances in Physics* (2008).
 G. Basile et al. *Eur. Phys. J.* (2007).
 L. Yang et al. *Phys. Rev. E* (2006).
 L. Delfini et al. *Phys. Rev. E* (2006).
 S. Lepri et al. *Chaos* (2005).
 J. Wang et al., *Phys. Rev. Lett.* (2004).
 S. Lepri et al. *Phys. Rep.* (2003).
 R. Livi and S. Lepri. *Nature* (2003).
 O. Narayan et al., *Phys. Rev. Lett.* (2002).
 A. Dhar. *Phys. Rev. Lett.* (2001).
 A. Lepri and R. Livi, *J. Stat. Phys.* (2000).
 T. Pozen et al., *Phys. Rev. Lett.* (2000).
 S. Lepri et. al. *Europhys. Lett.* (1998).



Prior Knowledge from Carbon Nanotubes – Experiment

RAPID COMMUNICATIONS

PHYSICAL REVIEW B

VOLUME 59, NUMBER 4

15 JANUARY 1999-II

Thermal conductivity of single-walled carbon nanotubes

J. Hone, M. Whitney, C. Piskoti, and A. Zettl

Department of Physics, University of California at Berkeley, Berkeley, California 94720 and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720 (Received 15 October 1998)

A room-temperature thermal conductivity of 1750-5800 W/m-K (the range derived above for the longitudinal thermal conductivity of a single rope) implies that $\kappa(30 \text{ K}) \sim 60-180$ W/m-K, and that $l \sim 0.5-1.5 \mu$ m. The ropes in the sample are generally a few microns long, although individual nano-tubes are generally observed to be $\sim 1 \mu$ m; both values are of the same order of magnitude as the range of mean free paths derived above.



Prior Knowledge from Carbon Nanotubes – Computations

VOLUME 84, NUMBER 20

PHYSICAL REVIEW LETTERS

15 May 2000

Unusually High Thermal Conductivity of Carbon Nanotubes

Savas Berber, Young-Kyun Kwon,* and David Tománek

Department of Physics and Astronomy, and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1116 (Received 23 February 2000)



Our results suggest an unusually high value $\lambda \approx 6600 \text{ W/m K}$ for an isolated (10, 10) nanotube at room temperature, comparable to the thermal conductivity of a hypothetical isolated graphene monolayer or graphite.

FIG. 3. Thermal conductivity λ for a (10, 10) carbon nanotube (solid line), in comparison to a constrained graphite monolayer (dash-dotted line), and the basal plane of AA graphite (dotted line) at temperatures between 200 and 400 K. The inset reproduces the graphite data on an expanded scale.



Raman Spectroscopy of Graphene

Visualization on Si/SiO₂ substrates



Other techniques:

- \rightarrow low-temperature transport study
- →cross-sectional TEM
- \rightarrow few other costly methods

D band: A_{1g} (~1350 cm⁻¹); *G* peak: E_{2g}; 2D band



A.C. Ferrari et al., *Phys. Rev. Lett.* 97, 187401 (2006).
I. Calizo, et al., *Nano Lett.*, 7, 2645 (2007).



Temperature Shift of the Raman G Peak in Graphene

Note: the sign is negative





N. Mounet et al, Phys. Rev. B 71, 205214 (2005).

Lifshits Membrane Effect:

И.М. Лифшиц, Журнал Экспериментальной и Теоретической Физики (1952)

Phonon frequency downshift with temperature is unusual when the bond-bond distances shorten with temperature since normally lattice contraction leads to the upward shift of the frequencies.



Temperature Effects on the Phonon Frequencies in Graphene



Computational data: Prof. Nicola Marzari, MIT

Raman spectrometer as thermometer



N. Bonini et al., *Phys. Rev. Lett.*, **99**, 176802 (2007). N. Bonini et al., *phys. stat. sol. (b)*, **245**, 2149 (2008)

Optothermal technique for measuring thermal conductivity \rightarrow





Converting Raman Spectrometer to Thermometer – The Plan of the Experiment

D band: A_{1g} (~1350 cm⁻¹); *G* peak: E_{2g}; 2*D* band







IEEE Spectrum illustration of the first measurements of thermal conductivity of graphene carried out at UC Riverside.

Details: A.A. Balandin et al., *Nano Letters*, 8, 902 (2008); A.A. Balandin, *Nature Mat.*, 10, 569 (2011).



Optothermal Measurement of Graphene Thermal Conductivity



Bilayer graphene ribbon bridging $3-\mu m$ trench in Si/SiO₂ wafer

 $K = (L/2a_GW)\chi_G(\Delta\omega/\Delta P_G)^{-1}.$ Connect $\Delta P_D \leftarrow \Rightarrow \Delta P_G$ through calibration \rightarrow Laser acts as a heater: ΔP_G

- → Raman "thermometer": $\Delta T_G = \Delta \omega / \chi_G$
- → Thermal conductivity: $K=(L/2a_GW)(\Delta P_G/\Delta T_G)$



A.A. Balandin, et al., *Nano Letters*, **8**, 902 (2008) – cited 9684 as of May 2019 2019 Brillouin Lecture - Alexander A. Balandin, University of California - Riverside



Evolution of the Intrinsic Thermal Conductivity in Low-Dimensional Systems

Experiment and Umklapp Scattering Theory



S. Ghosh, W. Bao, D.L. Nika, S. Subrina, E.P. Pokatilov, C.N. Lau and A.A. Balandin, "Dimensional crossover of thermal transport in fewlayer graphene," *Nature Materials*, **9**, 555 (2010).



W.-R. Zhong et al., Appl. Phys. Lett., 98, 113107 (2011).

Consistent with the prediction:

S. Berber, Y.-K. Kwon, and D. Tomanek, *Phys. Rev. Lett.*, **84**, 4613 (2000).



Comparison with Independent Experimental and Theoretical Studies



L. Lindsay, et al., *Phys. Rev. B*, **82**, 161402R (2010).

S. Chen, et al., ACS Nano, 5, 321 (2011).

- → Experimental thermal conductivity is above bulk graphite
- \rightarrow Theoretical thermal conductivity of graphene: ~2500 W/mK at RT for L=3 μm
- Theoretical value is size dependent and the ballistic limit for graphene: ~12800 W/mK
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Relative Contribution of Different Phonon Modes to Thermal Transport





Klemens Model of Heat Conduction: Bulk Graphite vs. Graphene





The Role of the Long-Wavelength Phonons in Heat Transport in Graphene

Thermal conductivity in graphene:

$$K \propto \frac{1}{\omega_m} \int_{\omega_c}^{\omega_m} \frac{d\omega}{\omega} \propto \frac{1}{\omega_m} \ln \left(\frac{\omega_m}{\omega_c} \right).$$

Graphene:



MFP = L - physical size of the system

 \rightarrow Limitation on MFL: $L=\tau v_s$

$$\tau_{U,s} = \frac{1}{\gamma_s^2} \frac{M \upsilon_s^2}{k_B T} \frac{\omega_{s,\text{max}}}{\omega^2}$$

→ Limiting low-bound frequency:

$$\omega_{s,\min} = \frac{\upsilon_s}{\gamma_s} \sqrt{\frac{M\upsilon_s}{k_B T} \frac{\omega_{s,\max}}{L}}$$

$$K = (2\pi\gamma^{2})^{-1} \rho(\upsilon^{4} / f_{m}T) \ln(f_{m} / f_{B}),$$

$$f_{B} = \left(M\upsilon^{3} f_{m} / 4\pi\gamma^{2} k_{B}TL\right)^{1/2}$$



Uniqueness of Heat Conduction in Graphene

Breakdown of Fourier's Law vs. Size-Dependent Intrinsic Thermal Conductivity

The phonon transport in graphene is 2D all the way down to zero frequency

Low-bound cut-off frequency is defined by the condition that the phonon MFP can not exceed the physical size of the graphene flake:

$$\omega_{s,\min} = \frac{\upsilon_s}{\gamma_s} \sqrt{\frac{M\upsilon_s}{k_B T} \frac{\omega_{s,\max}}{L}}$$





D.L. Nika, S. Ghosh, E.P. Pokatilov, A.A. Balandin, *Appl. Phys. Lett.*, **94**, 203103 (2009).



ARTICLE

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Length-dependent thermal conductivity in suspended single-layer graphene

Xiangfan Xu^{1,2,3,†}, Luiz F.C. Pereira^{4,†}, Yu Wang⁵, Jing Wu^{1,2}, Kaiwen Zhang^{1,2,6}, Xiangming Zhao^{1,2,6}, Sukang Bae⁷, Cong Tinh Bui⁸, Rongguo Xie^{1,6,9}, John T.L. Thong^{9,8}, Byung Hee Hong¹⁰, Kian Ping Loh^{2,8,11}, Davide Donadio⁴, Baowen Li^{1,2,6,8} & Barbaros Özyilmaz^{1,2,3,8}







Letter

Thermal Conductivity of Graphene and Graphite: Collective Excitations and Mean Free Paths

Giorgia Fugallo,^{*,†,‡} Andrea Cepellotti,^{‡,§} Lorenzo Paulatto,[†] Michele Lazzeri,[†] Nicola Marzari,^{‡,§} and Francesco Mauri[†]





Figure 4. Lattice thermal conductivity as a function of temperature for different grain size dimensions of single-layer naturally occurring polycrystalline graphene (98.9 12 C and 1.1 13 C).

Figure 7. Thermal conductivity as a function of temperature for naturally occurring graphene (black)

For graphene, we point out that a meaningful value of intrinsic thermal conductivity at room temperature can be obtained only for sample sizes of the order of 1 mm, something not considered previously.



Phonon Transport in Isotopically Engineered Graphene



¹³C and ¹²C difference:

~ 64 cm⁻¹

 $\omega \propto M^{-1/2}$

S. Chen, Q. Wu, C. Mishra, J. Kang, H. Zhang, K. Cho, W. Cai, A.A. Balandin and R.S. Ruoff, "Thermal conductivity of isotopically modified graphene," *Nature Materials*, 11, 203 (2012).



Phonon Engineering by Twisting





Thermal Conductivity of Twisted BLG



From graphene to other twisted van der Waals materials



Effects of the Defects Introduced by Electron Beam Irradiation



²⁰¹⁹ Brillouin Lecture - Alexander A. Balandin, University of California - Riverside



Part II: Thermal Management with Graphene



Source: the composite image consists of photos available on Internet



Thermal Interface Materials



→ Conventional TIMs: K=1-5 W/mK at the volume fractions *f* of filler ~50% at room temperature

$$R_{effective} = \frac{BLT}{k_{TIM}A} + R_{c_1} + R_{c_2}$$

→ Companies need K=10-30 W/mK

Current TIM based on polymer, grease filled with silver, alumina require 50-70% loading to achieve 1-5 W/mk.



Graphene Enhanced TIMs

Definitions: "graphene" vs. FLG vs. thin film of graphite



K.M.F. Shahil and A.A. Balandin, "Graphene - multilayer graphene nanocomposites as highly efficient thermal interface materials," *Nano Letters*, 12, 861 (2012).



Graphene Thermal Interface Materials



Y.-X. Fu et al. / International Journal of Thermal Sciences 86 (2014) 276-283



Composites with High Loading of Graphene and Boron Nitride





Thermal Percolation Threshold



Thermal conductivity of the epoxy composites with (a) graphene and (b) h-BN fillers. The thermal conductivity depends approximately linear on the loading fraction till $f_T \approx 30$ vol.% in graphene composites and $f_T \approx 23$ vol.% in h-BN composites. The maximum thermal conductivity enhancements of x51 and x24 are achieved for the epoxy composites with graphene (f=43 vol.%) and h-BN (f=45 vol.%), respectively.



Thermal Percolation Threshold in Graphene Composites



The semi-empirical model of Lewis-Nielsen:

 $K/K_m = (1 + ABf)/(1 - B\psi f)$

A depends on the shape of the fillers and their orientation with respect to the heat flow.

The parameter *B* takes into account the relative thermal conductivity of the two phases: the fillers (K_f) and the base matrix (K_m) , respectively.

 $\psi = 1 + ((1 - \phi_m)/\phi_m^2)f$

This parameter relates to the maximum packing fraction (ϕ_m) of the fillers.

The *apparent* thermal conductivity values of $K_f \sim 37 \text{ Wm}^{-1} \text{K}^{-1}$ and $K_f \sim 16 \text{ Wm}^{-1} \text{K}^{-1}$ have been extracted for graphene and *h*-BN fillers, respectively. 37



Dual Function of Graphene Composites: EMI Shielding and Thermal Management



Reflection, absorption, and transmission coefficients of (a) pristine epoxy; (b) epoxy with 5 wt% graphene and (c) epoxy with 50 wt% graphene.

At the graphene loading of 50 wt%, only 0.002% of EM power is transmitted through the composite while most of the energy is reflected from the surface.

(d) Comparison of the reflection, absorption, and the total shielding efficiency of pristine epoxy, epoxy with 30 wt% graphene and epoxy with 50 wt% graphene at the frequency of 8.2 GHz.

At the graphene loading of 50 wt%, the total shielding efficiency of the composite exceeds 45 dB. 38



TIMs with Oriented Graphene Fillers













Testing Graphene TIMs in Real-Life Conditions



TIMs with different concentration of graphene (left); graphene TIM applied to CPU (bottom left); CPU attached to the heat sink (bottom)





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Practical Testing of Graphene Enhanced TIMs in Desktop Computers



J. Renteria et al., Magnetically-functionalized self-aligning graphene fillers for high-efficiency thermal management applications, Materials and Design 88, 214–221 (2015)

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Hybrid Graphene – Paraffin PCM for Li-Ion Batteries



P. Goli, et al., "Graphene-enhanced hybrid phase change materials for thermal management of Li-ion batteries," J. Power Sources, 248, 37 (2014).



Graphene Coatings - Quilts - for GaN Devices



GaN HFETs were used as examples of high-power density transistors; PMMA was utilized as the supporting membrane for graphene transfer to a desired location; the alignment was achieved with the help of a micromanipulator

Z. Yan, G. Liu, J.M. Khan and A.A. Balandin, Graphene-Graphite Quilts for Thermal Management of High-Power Transistors, *Nature Communications* (2012).



Reduction of the Hot-Spot Temperature



The hot-spots temperature near drain contacts can be lowered by as much as ~ 20°C in such devices operating at ~13-W/mm – translates to an order of magnitude improvement in MTTF 2019 Brillouin Lecture - Alexander A. Balandin, University of California - Riverside



Graphene Laminate Coating



Cooperation with Professor Konstantin Novoselov, University of Manchester

H. Malekpour, K.-H. Chang, J.-C. Chen, C.-Y. Lu, D.L. Nika, K.S. Novoselov and A.A. Balandin, "Thermal conductivity of graphene laminate," Nano Lett., 14, 5155–5161 (2014).



Thermal Conductivity of Graphene Laminate: Scaling with the Flake Size and Orientation



2300 W/mK

Thermal properties of graphene and nanostructured carbon materials

1 W/mK

Alexander A. Balandin

Polycrystalline 3000 W/mK Single Crystal Diamond: sp³ Diamond: sp³ **RT Thermal Conductivity** of Carbon Materials: UNCD NCD MCD 3D CNT: sp² grain size decrease purity increase quasi-1D Diamond: 1000 – 2200 W/mK Graphite: 20 – 2000 W/mK DLC: Intrinsic Graphene: sp² in-plane DLC: 0.1 – 10 W/mK cross-plane sp²/sp³ 2D Graphite: sp² *a*-C: 0.01 – 1 W/mK layer size L increase density 3D NCD-MCD: 1 – 1000 W/mK quality increase and theoretical intrinsic 10 W/mK grain size increase $K \sim ln(L)$ CNTs: 1000 – 3500 W/mK 0.1 W/mK **Extrinsic Graphene** Graphene: 2000 – 5000 a-C interface or edge W/mK 100 W/mK scattering increase 0.01 W/mK 2000 W/mK

1000 W/mK



Conclusions

- → Thermal conductivity of graphene reveals unusual size-dependent phenomenon – different from ballistic transport
- → Few-layer graphene is an excellent system to study phonons in lowdimensions
- \rightarrow Few-layer graphene can be used as fillers in thermal composites
- Demonstrated thermal percolation in graphene composites and thermal conductivity of ~12 W/mK (SRC recent target: 10 W/mK)
- → Optimization of graphene composites (length scales, aspect ratios, orientation, composition) can bring revolutionary changes to TIMs
- Multi-functional composites with graphene: example of EMI shielding and thermal management

PHYSICS TODAY

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4 Mar 2011 in People & History

Obituary of Evgenii Pokatilov

Manuel Cardona (Max Planck Institute for Solid State Research, Stuttgart) Stepan I. Beril (State University of Pridnestrovie, Tiraspol) Vladimir M. Fomin (Institute for Integrative Nanosciences, IFW, Dresden) Alexander A. Balandin (University of California, Riverside)





Dr. Evgenii Petrovich Pokatilov, distinguished professor of physics at the Moldova State University, corresponding member of the Academy of Sciences of Moldova and member of the Russian Academy of Natural Sciences (RANS), died of a cancer on February 1, 2011 at the age of 84.



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