



Scientific Background on the Nobel Prize in Physics 2010

## GRAPHENE

compiled by the Class for Physics of the Royal Swedish Academy of Sciences

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# Graphene

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## 1. A new class of materials

Two-dimensional (2D) crystalline materials have recently been identified and analyzed.<sup>1</sup> The first material in this new class is graphene, a single atomic layer of carbon. This new material has a number of unique properties, which makes it interesting for both fundamental studies and future applications.

The electronic properties of this 2D-material leads to, for instance, an unusual quantum Hall effect.<sup>2,3</sup> It is a transparent conductor<sup>4</sup> which is one atom thin. It also gives rise to analogies with particle physics, including an exotic type of tunneling<sup>5,6</sup> which was predicted by the Swedish physicist Oscar Klein.<sup>7</sup>

In addition graphene has a number of remarkable mechanical and electrical properties. It is substantially stronger than steel, and it is very stretchable. The thermal and electrical conductivity is very high and it can be used as a flexible conductor.

The Nobel Prize in Physics 2010 honours two scientists, who have made the decisive contributions to this development. They are **Andre K. Geim** and **Konstantin S. Novoselov**, both at the University of Manchester, UK. They have succeeded in producing, isolating, identifying and characterizing graphene.<sup>1,8</sup>

## 2. Different forms of carbon

Carbon is arguably the most fascinating element in the periodic table. It is the base for DNA and all life on Earth. Carbon can exist in several different forms. The most common form of carbon is graphite, which consists of stacked sheets of carbon with a hexagonal structure. Under high pressure diamond is formed, which is a metastable form of carbon.

A new form of molecular carbon are the so called fullerenes<sup>9</sup>. The most common, called C<sub>60</sub>, contains 60 carbon atoms and looks like a football (soccer ball) made up from 20 hexagons and 12 pentagons which allow the surface to form a sphere. The discovery of fullerenes was awarded the Nobel Prize in Chemistry in 1996.

A related quasi-one-dimensional form of carbon, carbon nanotubes, have been known for several decades<sup>10</sup> and the single walled nanotubes since 1993.<sup>11,12</sup> These can be formed from graphene sheets which are rolled up to form tubes, and their ends are half spherical in the same way as the fullerenes. The electronic and mechanical properties of metallic single walled nanotubes have many similarities with graphene.

It was well known that graphite consists of hexagonal carbon sheets that are stacked on top of each other, but it was believed that a single sheet could not be produced in isolated form such that electrical measurements could be performed. It, therefore, came as a surprise to the physics community when in October 2004, Konstantin Novoselov, Andre Geim and their collaborators<sup>1</sup> showed that such a single layer could be isolated and transferred to another substrate and that electrical characterization could be done on a few such layers. In July 2005 they published electrical measurements on a single layer.<sup>8</sup> The single layer of carbon is what we call graphene.

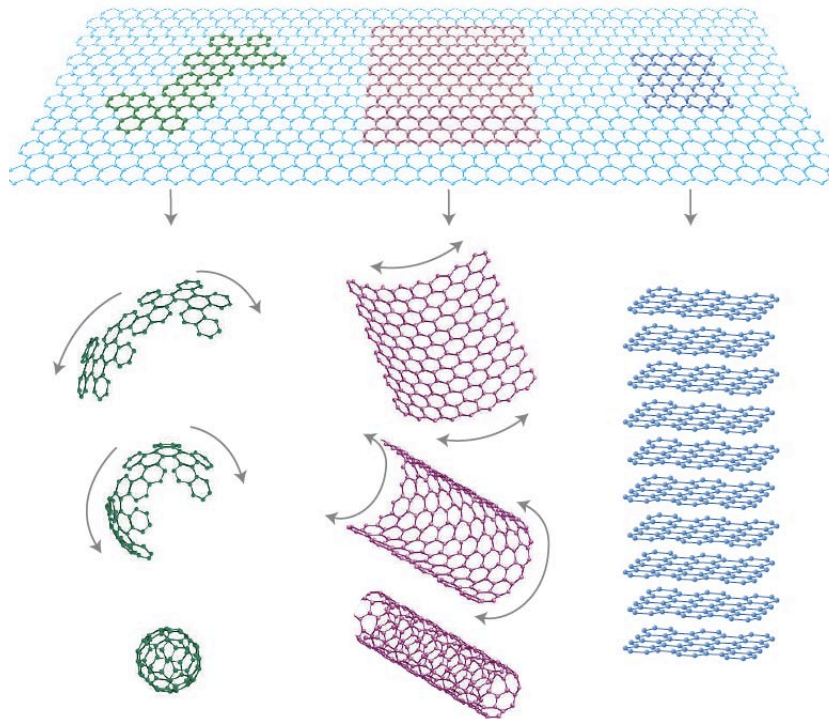


Figure 1. C60 fullerene molecules, carbon nanotubes, and graphite can all be thought of as being formed from graphene sheets, *i.e.* single layers of carbon atoms arranged in a honeycomb lattice.<sup>13</sup>

It should be mentioned that graphene-like structures were already known of since the 1960's<sup>14-17</sup> but there were experimental difficulties in isolating single layers in such a way that electrical measurements could be performed on them, and there were doubts that this was practically possible.

It is interesting to consider that everyone who has used an ordinary pencil has probably produced graphene-like structures without knowing it. A pencil contains graphite, and when it is moved on a piece of paper, the graphite is cleaved into thin layers that end up on the paper and make up the text or drawing that we are trying to produce. A small fraction of these thin layers will contain only a few layers or even a single layer of graphite, *i.e.* graphene.

Thus, the difficulty was not to fabricate the graphene structures, but to isolate sufficiently large individual sheets in order to identify and characterize the graphene and to verify its unique two-dimensional (2D) properties. This is what Geim, Novoselov, and their collaborators succeeded in doing.

### 3. What is graphene?

Graphene is a single layer of carbon packed in a hexagonal (honeycomb) lattice, with a carbon-carbon distance of 0.142 nm. It is the first truly two-dimensional crystalline material and it is representative of a whole class of 2D materials including for example single layers of Boron-Nitride (BN) and Molybdenum-disulphide (MoS<sub>2</sub>), which have both been produced after 2004.<sup>8</sup>

The electronic structure of graphene is rather different from usual three-dimensional materials. Its Fermi surface is characterized by six double cones, as shown in *Figure 2*. In intrinsic (undoped) graphene the Fermi level is situated at the connection points of these cones. Since the density of states of the material is zero at that point, the electrical conductivity of intrinsic graphene is quite low and is of the order of the conductance quantum  $\sigma \sim e^2/h$ ; the exact prefactor is still debated. The Fermi level can however be changed by an electric field so that the material becomes either n-doped (with electrons) or p-doped (with holes) depending on the polarity of the applied field. Graphene can also be doped by adsorbing, for example, water or ammonia on its surface. The electrical conductivity for doped graphene is potentially quite high, at room temperature it may even be higher than that of copper.

Close to the Fermi level the dispersion relation for electrons and holes is linear. Since the effective masses are given by the curvature of the energy bands, this corresponds to zero effective mass. The equation describing the excitations in graphene is formally identical to the Dirac equation for massless fermions which travel at a constant speed. The connection points of the cones are therefore called Dirac points. This gives rise to interesting analogies between graphene and particle physics, which are valid for energies up to approximately 1 eV, where the dispersion relation starts to be nonlinear. One result of this special dispersion relation, is that the quantum Hall effect becomes unusual in graphene, see *Figure 4*.

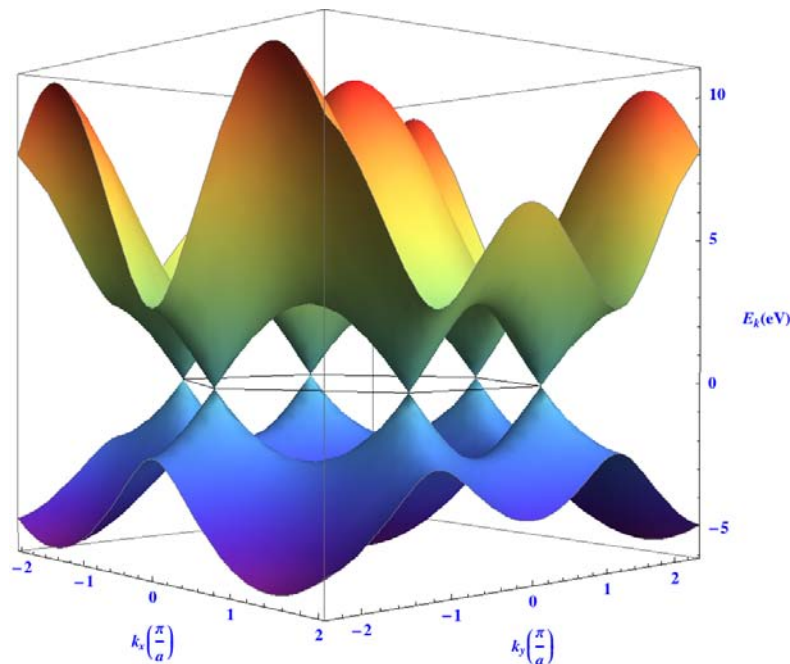


Figure 2. The energy,  $E$ , for the excitations in graphene as a function of the wave numbers,  $k_x$  and  $k_y$ , in the x and y directions. The black line represents the Fermi energy for an undoped graphene crystal. Close to this Fermi level the energy spectrum is characterized by six double cones where the dispersion relation (energy versus momentum,  $\hbar k$ ) is linear. This corresponds to massless excitations.

Graphene is practically transparent. In the optical region it absorbs only 2.3% of the light. This number is in fact given by  $\pi \alpha$ , where  $\alpha$  is the fine structure constant that sets the strength of the electromagnetic force. In contrast to low temperature 2D systems based on semiconductors, graphene maintains its 2D properties at room temperature. Graphene also has several other interesting properties, which it shares with carbon nanotubes. It is substantially stronger than steel, very stretchable and can be used as a flexible conductor. Its thermal conductivity is much higher than that of silver.

#### 4. The discovery of graphene

Graphene had already been studied theoretically in 1947 by P.R. Wallace<sup>18</sup> as a text book example for calculations in solid state physics. He predicted the electronic structure and noted the linear dispersion relation. The wave equation for excitations was written down by J.W. McClure<sup>19</sup> already in 1956, and the similarity to the Dirac equation was discussed by G.W. Semenoff in 1984,<sup>20</sup> see also DiVincenzo and Mele.<sup>21</sup>

It came as a surprise to the physics community when Andre Geim, Konstantin Novoselov and their collaborators from the University of Manchester (UK), and the Institute for Microelectronics Technology in Chernogolovka (Russia), presented their results on graphene structures. They published their results in October of 2004 in Science.<sup>1</sup> In this paper they described the fabrication, identification and Atomic Force Microscopy (AFM) characterization of graphene. They used a simple but effective mechanical exfoliation method for extracting thin layers of graphite from a graphite crystal with Scotch tape and then transferred these layers to a silicon substrate. This method was first suggested and tried by R. Ruoff's group<sup>22</sup> who were, however, not able to identify any monolayers. The Manchester group succeeded by using an optical method with which they were able to identify fragments made up of only a few layers. An AFM picture of one such sample is shown in Figure 3. In some cases these flakes were made up of a single layer, *i.e.* graphene was identified. Furthermore, they managed to pattern samples containing only a few layers of graphene into a Hall bar and connect electrodes to it.

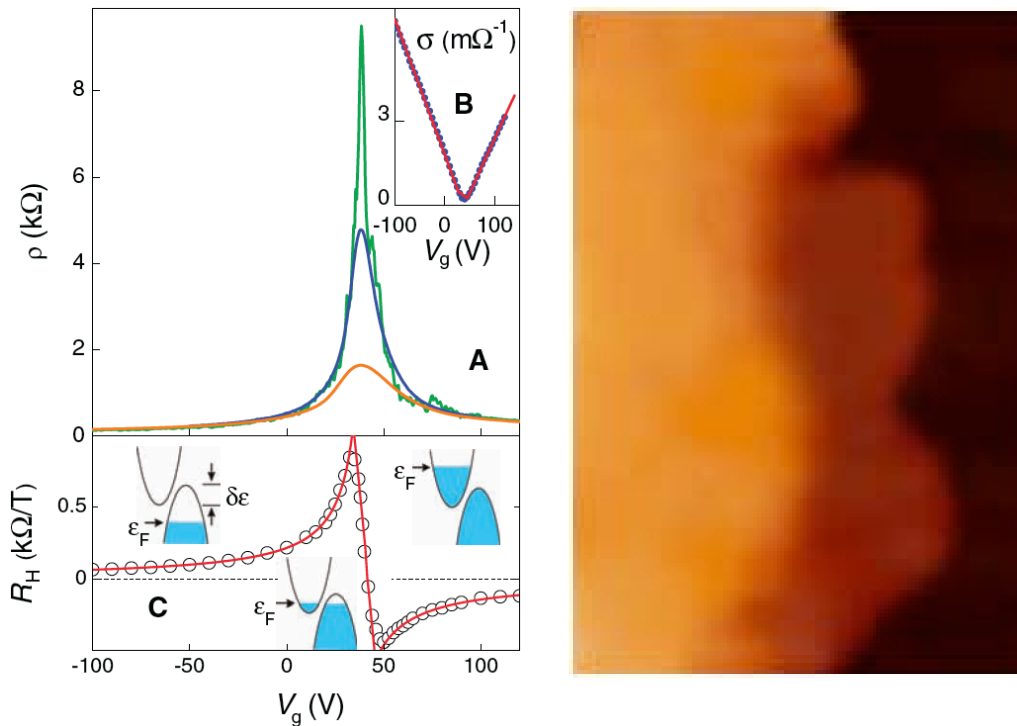


Figure 3. (Left) A) The (longitudinal) resistivity of a few layer graphene sample for three different temperatures (5K green, 70K blue, 300K orange), note the ambipolar dependence on gate voltage. B) The conductance as a function of gate voltage at 77K. C) The Hall resistivity as a function gate voltage for the same sample.<sup>1</sup>(Right) Atomic Force Microscopy (AFM) picture of a monolayer of graphene. The black area is the substrate, the dark orange is a mono layer of graphene and has a thickness of  $\sim 0.5\text{nm}$ , the bright orange part contains a few layers and has a thickness of  $\sim 2\text{nm}$ .<sup>23</sup>

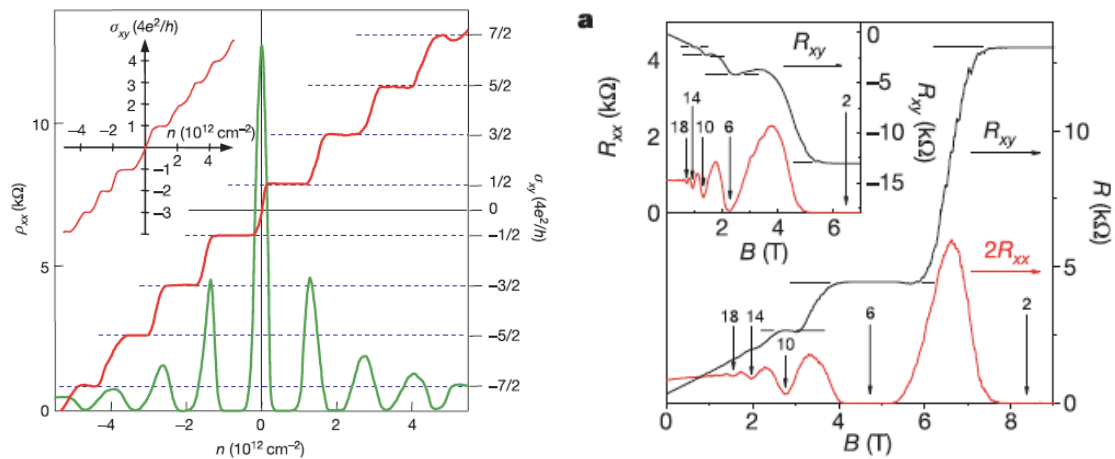


Figure 4 Experimental observation of the unusual quantum Hall effect in graphene. (Left) The Hall conductivity (red) and the longitudinal resistivity (green) as a function of carrier density. The inset shows the Hall conductivity for bi-layer graphene. Note that the spacing between plateaus for graphene is  $4e^2/h$ , i.e. bigger than for the usual quantum Hall effect and that the steps occur at half integer multiples of this value. For a bilayer of graphene the step height is the same, but the steps occur at integer multiples of  $4e^2/h$  but with no step at zero density.<sup>2</sup> (Right) The longitudinal and Hall resistance as a function of magnetic flux density for an electron doped sample. The inset shows the same data for a hole doped sample.<sup>3</sup>



In this way they were able to measure both the (longitudinal) resistance and the Hall resistance. An important piece of data was the ambipolar field effect where the resistance was measured as a function of an electric field applied perpendicular to the sample. The data are shown in *Figure 3*. The sheet resistivity has a clear maximum, and falls off on both sides of the maximum. This indicates increased doping of electrons to the right and of holes to the left of the maximum. Note that the maximum sheet resistivity is  $\sim 9 \text{ k}\Omega$ , which is of the order of the quantum of resistance.

Once the technology to fabricate, identify, and attach electrodes to the graphene layers was established, both the Manchester group and other groups quickly made a large number of new experiments.<sup>2,3,8,24,25</sup> These included studies of the unusual quantum Hall effect, and also the preparation of other 2D crystalline materials such as monolayers of BN.

Apart from the exfoliation method, different ways of growing very thin carbon films were also studied, in particular by a group led by W.A. de Heer at Georgia Tech. They were refining a method to burn off silicon from a Silicon Carbide (SiC) surface, leaving a thin layer of carbon behind. This is done by heating the SiC crystal to approximately  $1300 \text{ }^\circ\text{C}$ . The method had been used by several groups before,<sup>15,16</sup> but those early studies concentrated on surface science and there were no transport measurements. In December of 2004, just two months after the paper by Novoselov *et al.* was published, de Heer's group published their first paper on transport measurements on thin carbon films.<sup>26</sup> They presented magneto-resistance measurements and also a weak electric field effect. de Heer and his collaborators also hold a patent on how to fabricate electronic devices from thin layers of carbon.<sup>27</sup>

A group at the University of Columbia led by P. Kim investigated an alternative approach for making thin carbon layers. They attached a graphite crystal to the tip of an atomic force microscope and dragged it along a surface. In this way they were able to produce thin layers of graphite down to approximately 10 layers.

As mentioned above, the nonlinear dispersion relation gives rise to an unusual quantum Hall effect. This was demonstrated independently by two groups, the Manchester group and the group led by P. Kim; both groups were now using the exfoliation method. The two papers were published back-to-back in the same issue of *Nature* in November of 2005. The data can be seen in *Figure 4*.

Since 2005 development in this research area has literally exploded, producing an increasingly growing number of papers concerning graphene and its properties. Double layers of graphene, which have different properties compared to (single layer) graphene have been studied thoroughly.<sup>28-32</sup> Studies at higher magnetic fields have been performed to investigate the fractional quantum Hall effect in graphene.<sup>33,34</sup> Furthermore mechanical studies of graphene have shown that it is mechanically extremely strong, a hundred times stronger than the strongest steel.<sup>35</sup> Another important discovery was that light absorption in graphene is related to the fine structure constant as mentioned above.<sup>36</sup>

There have also been a number of important papers describing the analogies to particle physics based on the Dirac equation. The formal similarity between the excitations in graphene and two-dimensional Dirac fermions, has allowed testing of the so called Klein tunneling which was suggested by the Swedish physicist Oskar Klein<sup>7</sup>. This phenomenon

predicts that a tunnel barrier can become fully transparent for normal incidence of massless particles. Under certain conditions the transparency can also oscillate as a function of energy. That this could be tested in graphene was suggested by Katsnelson, Geim and Novoselov in 2006,<sup>5</sup> and verified by Young and Kim in 2009.<sup>6</sup>

## 5. Future applications

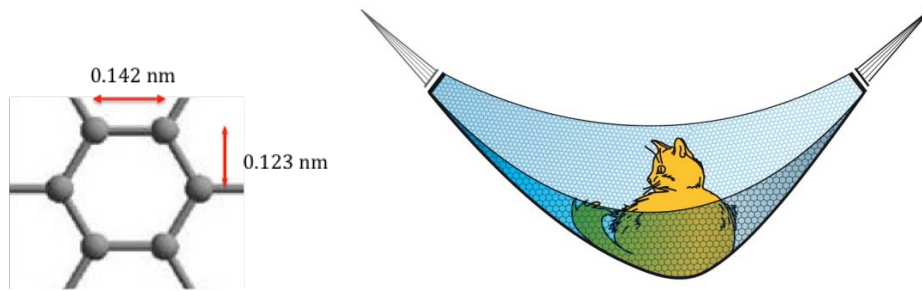
Graphene has a number of properties which makes it interesting for several different applications. It is an ultimately thin, mechanically very strong, transparent and flexible conductor. Its conductivity can be modified over a large range either by chemical doping or by an electric field. The mobility of graphene is very high<sup>30</sup> which makes the material very interesting for electronic high frequency applications.<sup>37</sup> Recently it has become possible to fabricate large sheets of graphene. Using near-industrial methods, sheets with a width of 70 cm have been produced.<sup>38,39</sup> Since graphene is a transparent conductor it can be used in applications such as touch screens, light panels and solar cells, where it can replace the rather fragile and expensive Indium-Tin-Oxide (ITO). Flexible electronics and gas sensors<sup>40,41</sup> are other potential applications. The quantum Hall effect in graphene could also possibly contribute to an even more accurate resistance standard in metrology.<sup>42</sup> New types of composite materials based on graphene with great strength and low weight could also become interesting for use in satellites and aircraft.<sup>43,44</sup>

## 6. Conclusion

The development of this new material, opens new exiting possibilities. It is the first crystalline 2D-material and it has unique properties, which makes it interesting both for fundamental science and for future applications. The breakthrough was done by Geim, Novoselov and their co-workers; it was their paper from 2004 which ignited the development. For this they are awarded the Nobel Prize in Physics 2010.



## Appendix, some properties of graphene



### **Density of graphene**

The unit hexagonal cell of graphene contains two carbon atoms and has an area of  $0.052 \text{ nm}^2$ . We can thus calculate its density as being  $0.77 \text{ mg/m}^2$ . A hypothetical hammock measuring  $1 \text{ m}^2$  made from graphene would thus weigh  $0.77 \text{ mg}$ .

### **Optical transparency of graphene**

Graphene is almost transparent, it absorbs only 2.3% of the light intensity, independent of the wavelength in the optical domain. This number is given by  $\pi \alpha$ , where  $\alpha$  is the fine structure constant. Thus suspended graphene does not have any color.

### **Strength of graphene**

Graphene has a breaking strength of  $42 \text{ N/m}$ . Steel has a breaking strength in the range of  $250\text{-}1200 \text{ MPa} = 0.25\text{-}1.2 \times 10^9 \text{ N/m}^2$ . For a hypothetical steel film of the same thickness as graphene (which can be taken to be  $3.35 \text{ \AA} = 3.35 \times 10^{-10} \text{ m}$ , *i.e.* the layer thickness in graphite), this would give a 2D breaking strength of  $0.084\text{-}0.40 \text{ N/m}$ . Thus graphene is more than 100 times stronger than the strongest steel.

In our  $1 \text{ m}^2$  hammock tied between two trees you could place a weight of approximately  $4 \text{ kg}$  before it would break. It should thus be possible to make an almost invisible hammock out of graphene that could hold a cat without breaking. The hammock would weigh less than one  $\text{mg}$ , corresponding to the weight of one of the cat's whiskers.

### **Electrical conductivity of graphene**

The sheet conductivity of a 2D material is given by  $\sigma = en\mu$ . The mobility is theoretically limited to  $\mu = 200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  by acoustic phonons at a carrier density of  $n = 10^{12} \text{ cm}^{-2}$ . The 2D sheet resistivity, also called the resistance per square, is then  $31 \text{ } \Omega$ . Our fictional hammock measuring  $1 \text{ m}^2$  would thus have a resistance of  $31 \text{ } \Omega$ .

Using the layer thickness we get a bulk conductivity of  $0.96 \times 10^6 \text{ } \Omega^{-1} \text{ cm}^{-1}$  for graphene. This is somewhat higher than the conductivity of copper which is  $0.60 \times 10^6 \text{ } \Omega^{-1} \text{ cm}^{-1}$ .

### **Thermal conductivity**

The thermal conductivity of graphene is dominated by phonons and has been measured to be approximately  $5000 \text{ Wm}^{-1} \text{ K}^{-1}$ . Copper at room temperature has a thermal conductivity of  $401 \text{ Wm}^{-1} \text{ K}^{-1}$ . Thus graphene conducts heat 10 times better than copper.

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