

# A. K. Geim (2011), *Nobel Lecture: Random walk to graphene*, *Reviews of Modern Physics*, **83**, 851

<https://journals.aps.org/rmp/pdf/10.1103/RevModPhys.83.851>

This week we're looking at a different style of paper: a review article. A review article is written to give an overview of a field or topic of research and so they're particularly useful if you're new to a field. They are written with a wider audience in mind and so generally start with less assumed knowledge of the reader, but they provide lots of references to the technical pieces that constitute the key research in a particular field. This review in particular is written for the widest possible audience since it is an adaptation of the speech given when Andre Geim and Konstantin Novoselov received the 2010 Nobel Prize for physics for their discovery of graphene. This article gives an insight into the life of scientist and how they became a Nobel Prize winner.

As with last week, take a brief skim read through the paper and make a list of some of its main points. Check you understand the key ideas by answering a few of what you consider to be the most important questions. As a suggestion, we think the key things you need to know to get the most out of this article are:

1. What is graphene?
2. What is microfabrication?
3. What is diamagnetism?
4. What is the electric field effect?

Either answer these 4 questions (or the ones you wrote) in as simple terms as possible after a little bit of research (remember to cross check what you find makes sense across more than one website).

Below are the questions to answer as you go along for each section – some of the sections we are going to skip so take note.

## *Zombie management*

(P1, C1) <i>'Web of Science soberly reveals that the papers were cited twice'</i> . What is a citation and why is it sobering that they were only cited twice?	A citation is a reference to a source. Every time a new journal article cites your work, it is counted up by large indexes to quantify how 'important' it is. It is certainly sobering to realise that five years work has amassed two citations in nearly 20years, but this is often the case with scientific research.
(P1, C1) What does Geim mean by the phrase 'zombie project'?	Research in a field that is dead and is no longer of consequence. It should be noted that research might be considered 'dead' at a particular time if there's little interest in it, but that doesn't mean it will remain this way in the future.
(P1, C1) Thinking back to week 3: <i>'the superconductor served only to condense an</i>	A type-II superconductor. Above their first critical field, a type-II superconductor will allow magnetic field lines to penetrate the bulk of the material, but only in the form of 'tubes' of quantised flux. A type-I superconductor in its superconducting state will

<p><i>external magnetic field into an array of vortices</i>'. What type of superconductor must this have been?</p> <p>(P1, C1) What does inhomogenous mean?</p> <p>(P1, C1) What is electron transport and why is it affected by a magnetic field?</p>	<p>never let a magnetic field penetrate its bulk (but does allow a magnetic field to penetrate on the surface a short way – the London penetration depth).</p> <p>Not uniform. As the magnetic field penetrates the superconductor in discrete regions, it demonstrates significant variations across the 'sandwich' device.</p> <p>Electron transport is simply the movement of electrons through a material (so movement on the macroscopic scale). It is affected by a magnetic field as a moving electron is a current, and around any current circulates a magnetic field. Therefore a moving electron is inherently magnetic and is affected by an applied magnetic field.</p>
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*One man's junk, another man's gold*

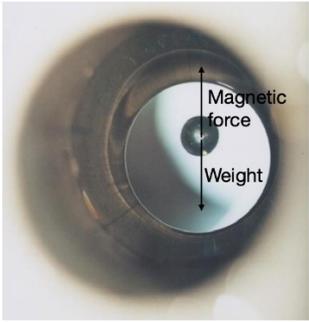
<p>(P1, C2) What does 'submicron' mean?</p> <p>(P1, C2) What is a '<i>h index</i>'?</p> <p>(P1, C2) What does mesoscopic mean? How does this link to Anderson's paper <i>More Is Different</i> from week one?</p> <p>(P1, C2) What is a 2D electron gas?</p>	<p>Something smaller than a micrometer (<math>1\ \mu\text{m}=1\times 10^{-6}\ \text{m}</math>) in size.</p> <p>It's a metric for comparing the research output of academics <a href="https://en.wikipedia.org/wiki/H-index">https://en.wikipedia.org/wiki/H-index</a> A 'h index' of 1 is low.</p> <p>Mesoscopic physics studies an intermediate scale of physics in between nanophysics (on the smaller side) and studies of materials on the micrometer scale (on the larger side). It's a realm of size where quantum mechanics begins to enter. This realm of physics is very much what Anderson was discussing when talking of emergence - the physics of systems that are on the transition between one scale (and one set of rules) and another (with a new set of rules).</p> <p>We can think of a 2D electron gas as a collection of electrons that are free to move around in a plane (hence 2D) but are confined from moving in the third dimension.</p>
<p>We are probably not familiar with all of the effects and techniques that Geim mentions – quantum point contacts, resonant tunneling, the quantum Hall effect, molecular beam epitaxy, electron-beam lithography etc. but that's okay. They're not crucial to our understanding of the article so we can ignore them for now. It takes time to realise which bits are important and which bits we can ignore for now – we just need to gain experience at reading papers.</p>	

*Dutch comfort*

<p>(P2, C1) Why would scientists want to study the individual vortices within a</p>	<p>Because the superconducting mechanism of type-II superconductors is still unknown. Scientists have been using experiments that approach the subject from every possible</p>
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<p>type-II superconductor (think back to week 3).</p>	<p>angle to try and understand why type-II superconductors become superconducting. Also, understanding these magnetic vortices could be important alone as they could have technological uses if they could be readily manipulated.</p>
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*A spell of levity*

<p>(P2, C2) In the first paragraph of 'a spell of levity' what does Geim highlight about the political nature of science?</p>	<p>That sometimes you have to do things to justify the existence of a facility/department. A lot of time and effort had gone into creating a 20T magnet, but it wasn't being used (at the time) to its full potential – it is used more regularly now as the focus of condensed matter research shifts over time.</p>
<p>(P2, C2) What advantage did Geim have in studying 'magnetic water'?</p>	<p>The strong magnetic field of the 20T magnet should make any 'magnetic water' effect much more prevalent than any standard magnet (whose field is typically 200times smaller).</p>
<p>(P2, C2) What is diamagnetism?</p>	<p>The effect of an external magnetic field acting on certain materials to create an opposing magnetic field within the material itself (these materials are called diamagnetic materials). This field is repelled by the original magnetic field.</p>
<p>(P2, C2) Why did the water 'float' inside the 20T magnetic field?</p>	<p>Water is a diamagnetic material. When an external field is applied to it, a magnetic field is created within the water in the opposite direction to the applied field. In the experimental setup that Geim had, the resulting repulsion was enough to balance the weight of small droplets of water.</p>
<p>(P2, C2) Draw a force diagram for a droplet of water inside Geim's magnetic field.</p>	
<p>(P2, C2) Why can't you see levitating water with a normal magnet?</p>	<p>Because the magnetic response of water is very weak (its magnetic susceptibility is <math>9.0 \times 10^{-6}</math>) and so a standard magnet is not strong enough to create a large enough magnetic force to counterbalance the weight.</p>
<p>(P3, C1) Why do you think a frog can also be levitated within a magnetic field?</p>	<p>Since a frog is mostly water (as are most living things), they also have a diamagnetic response. If we had a magnetic field large enough, you can levitate humans too.</p>

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*Friday night experiments*

<p>(P3, C2) A van der Waals force is an intermolecular force – what does this mean?</p> <p>(P3, C2) Van der Waals forces are incredibly weak. How can such weak forces manage to suspend a gecko?</p> <p>(P3, C2) Why would a large diamagnetic response be an indicator of possible superconductivity? (Think back to week three)</p>	<p>It's a force between different molecules (not forces within a single molecule which has the term intramolecular).</p> <p>The van der Waals force arises between the hairs on the gecko's feet and the surface it walks on. Whilst the force between a single hair and the surface is tiny (in the nN range), a gecko has millions of hairs and these forces add up.</p> <p>The Meissner effect in superconducting systems is a case of perfect diamagnetism as the applied magnetic field is prevented from penetrating the bulk. This is because superconducting currents are created on the surface which lead to an opposing magnetic field, shielding the bulk. So if we see a large diamagnetic response in a material, it may be because the material is superconducting and creating such opposing superconducting currents.</p>
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*Mancunian way*

<p>(P4, C1) How have Geim's previous experiences in research shaped his attitudes to spending his grant money?</p>	<p>Given that he's worked in situations where money has been tight and resources scant, he is more than happy to forgo new buildings or rooms or large infrastructure and instead spend his money on the necessary equipment to get results.</p>
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*Three little clouds*

<p>(P4, C2) In terms of free electrons, what is the difference between a metal and a semiconductor?</p> <p>(P4, C2) What is the electric field effect (also known as the field effect)?</p>	<p>A metal has free electrons that can conduct electricity and a current can run even with a very small potential difference. A semiconductor does not have free electrons unless a large enough potential difference is applied to it (think of the I-V curve of a LED).</p> <p>The alteration in electrical conductivity of a material through the application of an electric field. In a metal, the number of current carriers is large and so electric fields don't penetrate far into a material. In a semiconductor, though, the smaller number of carriers means that the electric field can penetrate further into the material and also alter the number of carriers on the surface of the semiconductor.</p>
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<p>(P4, C2) In terms of free electrons, what is the difference between a metal and a semiconductor?</p> <p>(P4, C2) In terms of the number of free electrons, what is the difference between a metal and a semimetal?</p> <p>(P5, C1) What is a carbon nanotube? What is its relationship to graphene?</p> <p>(P5, C1) What was Geim hoping to achieve by getting his student to look into thin films of graphite?</p>	<p>A metal has free electrons that can conduct electricity and a current can run even with a very small potential difference. A semiconductor does not have free electrons unless a large enough potential difference is applied to it (think of the I-V curve of a LED).</p> <p>Semimetals have fewer free electrons (a smaller 'carrier concentration') than metals. They don't have a threshold potential difference to conduct like semiconductors, but their conductivities aren't as large as metals.</p> <p>A carbon nanotube is a tube whose walls are one atomic layer thick and are entirely made of carbon atoms. A carbon nanotube can be considered to be a rolled up piece of graphene.</p> <div data-bbox="662 758 1097 982" data-label="Chemical-Block"> <p>The diagram illustrates the relationship between graphene and carbon nanotubes. On the left, a 'Graphene Sheet' is shown as a flat, two-dimensional lattice of carbon atoms arranged in a hexagonal pattern. An arrow labeled 'rolled up' points to the right, where a 'Carbon Nanotube' is shown as a cylindrical tube formed by rolling the graphene sheet. The tube's walls are composed of a single layer of carbon atoms.</p> </div> <p>His main aim was to look at the electric field effect in metals (even though he knew the effect would be very small). His secondary aim was to look at some of the unusual properties of graphite to try to better understand the material.</p>
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*Legend of Scotch tape*

<p>(P5, C1) What is pyrolytic graphite (or pyrolytic carbon) and what's its advantage over natural graphite when trying to produce graphene?</p> <p>(P5, C1) In polishing the sample, what were they hoping to achieve?</p> <p>(P5, C1) What might the advantage of highly oriented pyrolytic graphite be over the sample that they originally used?</p>	<p>Pyrolytic carbon is a manmade form of carbon which can be understood now as individual sheets of graphene with some covalent bonding between the sheets. Thus it is much easier to cleave pyrolytic carbon into graphene sheets compared to natural graphite which crystallises into randomly oriented small domains.</p> <p>To polish down a piece of the pyrolytic graphite to be as thin as possible (hopefully atomically thin).</p> <p>In HOPG, the crystallographic planes should be all in the same direction and the bonding between layers should be weaker than the high-density graphite (so that it's easier to form thin samples).</p>
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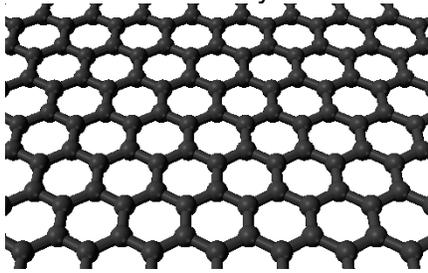
<p>(P5, C2) How does sellotape create thinner samples of graphite than polishing?</p>	<p>The sellotape can be used to simply peel away a layer of graphite from the larger sample. The bond formed between the graphite and the sellotape is stronger than the bond between one layer of graphite and the next, and this very gentle method allows you to simply isolate a very smaller number of layers of graphite.</p>
<p>(P5, C2) If you've read any Shakespeare, compare and contrast the styles of the bard with Geim in this article so far (this is not a serious question...).</p>	
<p>(P6, C1) What is a substrate in crystallography?</p>	<p>An underlying material which is used as a surface on which to place or grow a sample that you want to be flat.</p>
<p>(P6, C1) Why does being optically transparent indicate that a sample is thin?</p>	<p>The thinner a sample is, the more likely it is that photons will pass through without scattering from the material itself.</p>
<p>(P6, C1 and Figure 2d) Describe what is shown in Figure 2d.</p>	<p>In the centre of the image, the green blob with red lines is the sample of graphene (it's unclear whether this is atomically thin and therefore truly graphene). The four, brown crystalline looking objects are the four silver contacts that Geim discusses that have been attached to look at the electrical properties of the sample.</p>
<p>(P6, C1 and Figure 2d) 50µm is a difficult size to imagine. Find a comparison to understand how big 50µm is.</p>	<p>Human hairs lie in region of thickness between 20µm and 180µm so these samples are the width of thin hairs and not much longer. Imagine trying to attach four electrical contacts to a sample that has a width, thickness and height that are all comparable to a thin hair!</p>

*Eureka moment*

<p>(P6, C1) Rather than using sellotape to create graphene, what does Geim describe as his real Eureka moment?</p>	<p>After noticing the electric field effect in his crude samples of graphene, the Eureka moment was to imagine what could be done if he used the 'full arsenal of microfabrication facilities' to make samples.</p>
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<p>(P6, C2) In the simplest of terms, what does Geim mean when he talks about moving ‘from multilayers to monolayers and from hand-made to lithography devices’.</p>	<p>His samples had got thinner so they were now one layer thick instead of many layers and the electrical contacts were now made through more precise techniques (lithography).</p>
<p>(P6, C2) How did Geim and his team ensure that any of their conclusions about the electrical properties of graphene were valid?</p>	<p>They ensured that they were reproducible by only considering data that was consistent between many devices.</p>
<p>(P6, C2) Studying 50 samples doesn’t initially sound too taxing... why is it such hard work.</p>	<p>Because the samples are so small and fiddly and the measurements they are making are very precise.</p>
<p>(P6, C2) What does Geim highlight about the review process for getting articles published?</p>	<p>That it is hard work and not all referees agree with what constitutes an advancement in science.</p>

*Defiant existence*

<p>(P7, C1) What does Geim mean by a continuous monolayer?</p>	<p>In the case of graphene, a continuous monolayer is a piece of graphene (this is the monolayer part) that maintains a constant crystallographic structure over the size of the sample – the familiar hexagonal shape structure of graphene – rather than breaking up into different regions (called domains). Continuous monolayer:</p>  <p>In Figure 3, d, you can see how graphene might form little islands is different orientation if you look carefully at the largest blocks.</p>
<p>(P7, C1) Why does a system often prefer to small regions rather than a continuous layer?</p>	<p>To reduce its surface energy. Surface effects are incredibly unusual – just think about the way water can behave when it’s in small droplets (where it has a greater surface to volume ratio).</p>
<p>(P7, C1) Why was it predicted that small, flat</p>	

graphene sheets were unlikely to occur?	Because theory told us that the atoms should prefer to exist in a 3D structure to minimise their energy.
The third argument for why the existence of graphene is surprising is a little more involved so we won't dwell on it. To grow a sample, the atoms need cool into a stable arrangement. If we're trying to grow a 2D sample, this is problematic as thermal fluctuations have a greater effect. Combined with the need for a substrate to grow it on, this limits the predicted size of graphene samples.	
<p>(P7, C1) What is a theoretical disadvantage of graphene when it comes its existence in air?</p> <p>(P7, C1) Summarise (in as much detail as you feel comfortable with) the reasons that people would have been surprised that small, flat, continuous, monolayer sheets of graphene exist.</p>	It has two surfaces and would therefore seem to stand more chance of being reactive in ambient conditions

For our purposes, we can largely ignore the section *Graphene incarnations* (P8 and most of P9, C1), but you may wish to read it for your own interest.

*Planet graphene* (The Greek letters spell 'planet')

<p>(P9, C2) Why does Geim believe people were so interested in his paper?</p> <p>(P9, C2) Looking back, what is a typical value for the percentage change in the number of electronic carriers if a material displays the electric field effect?</p> <p>(P9, C2) What does 'charge carrier mobility' mean?</p> <p>(P9, C2) Why does Geim refer to 'ballistic transport' for graphene?</p>	<p>For the results of the electronic properties of graphene rather than the simpler fact of creating large monolayer samples of it.</p> <p>Around a 1% change in the number of carriers. Graphene surpasses this by a factor of 1000!</p> <p>How quickly a charge carrier can move through a material when propelled by an electric field.</p> <p>Because the carriers can travel without scattering (and so travel very quickly) – charge carrier scattering is the origin of a material's resistivity.</p>
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<p>(P9, C2) Summarise some of the remarkable electronic properties of graphene.</p>	<p>It shows a huge electric field effect – by altering the potential difference across the graphene, you can tune it from having so many electronic carriers that it seems to be metallic, to having so few that it looks like a semiconductor. Remember that previously, the electric field effect would only change the number of carriers by around 1% in other materials. The graphene sheet remained conducting regardless of the contacts and surface treatments and being left in ambient conditions. The surface of materials is renowned for being reactive and terrible at conducting when exposed to air, yet graphene (despite it all being on the surface) bucks this trend. Graphene has an incredibly high charge carrier mobility.</p>
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The section '*Magic of flat carbon*' gives some of the newer findings about graphene's capabilities. These are a little more specialized and aren't discussed in enough detail for us to truly understand so we'll leave our questions for this section.

*Ode to one*

<p>(P10, C1) Other than its electronic properties, in what other ways in graphene remarkable?</p>	<p>It displays an incredibly high strength. Graphene chemistry is made possible by its unusual bonding properties with other materials.</p>
<p>(P10, C2) Why is graphite (and bilayers of graphene) much weaker than monolayer graphene?</p>	<p>Because the layers can slide against one another. The inter-layer bonds are much weaker than the intra-layer bonds.</p>
<p>(P10, C2) What reason does Geim give for graphite (and multilayer graphene) having significantly different electronic properties?</p>	<p>Electric fields are screened by the electrons within graphite (and multilayer graphene) so that the electric field doesn't penetrate more than a couple of layers into the material. As graphene is just a single layer, there is no such screening.</p>

## **SUMMARY QUESTIONS**

What makes graphene such a momentous material?

Which piece of Geim's research stood out most to you? Summarise it in three sentences or less.

What have you learned about the workings of a scientific research group from this article?

Why do you think Geim believes that "*Chances of success are much higher where the field is new*"? Is there any reason why this might not be the case?

## **Further Reading**

More information on the levitation of frogs can be found here

<https://physicstoday.scitation.org/doi/pdf/10.1063/1.882437>

Discovery and characterisation of graphene (this is actually a paper in the journal *Science* but a version is available on the arXiv that does not require an academic subscription)

<https://arxiv.org/pdf/cond-mat/0410550.pdf>