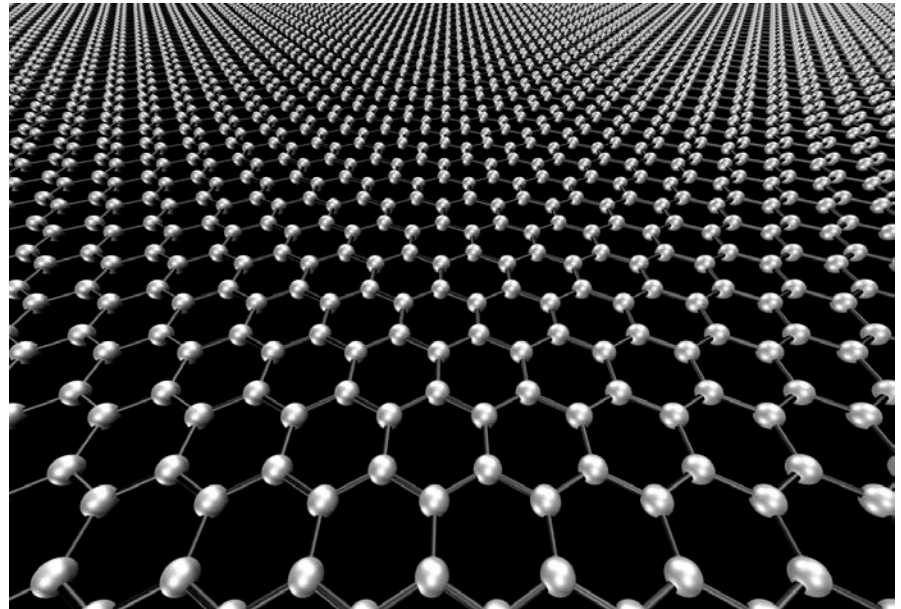


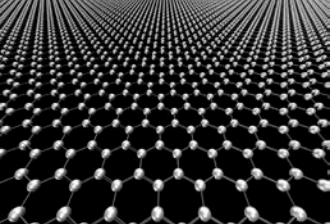
# "Grafen, nanomaterial starkare än stål, leviterande grodor, och en historik orättvisa?"

Kai Nordlund

27.1.2014

Institutionen för fysik  
Helsingfors universitet





# Kols kemiska bindningar

- Kol har 3 typer av kemisk bindning

- “sp”: linjär

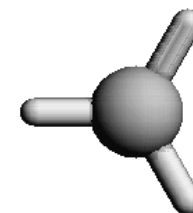
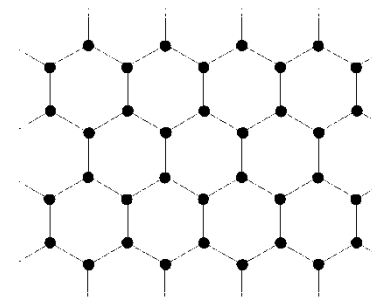
- T.ex. acetylen  $C_2H_2$



- “sp<sup>2</sup>”: 3 bindningar i planet, vinkeln 120°

- T.ex.. etylen  $C_2H_4$

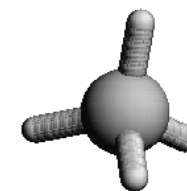
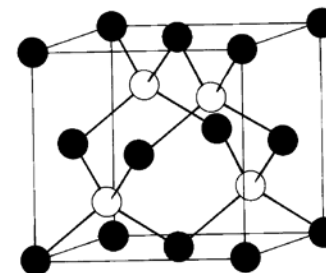
- Grafits bulkstruktur

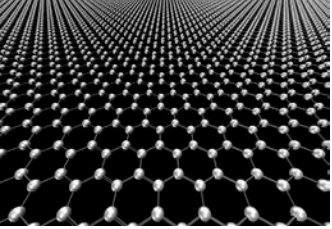


- “sp<sup>3</sup>”: 4 bindningar i 3D

- E.g. metan  $CH_4$

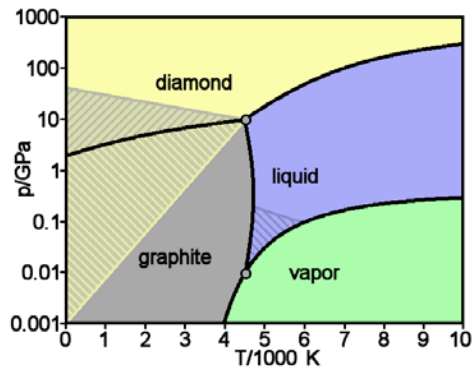
- Diamant-strukturen

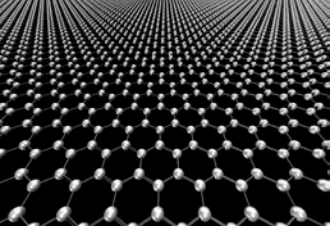




# Grafit och diamant

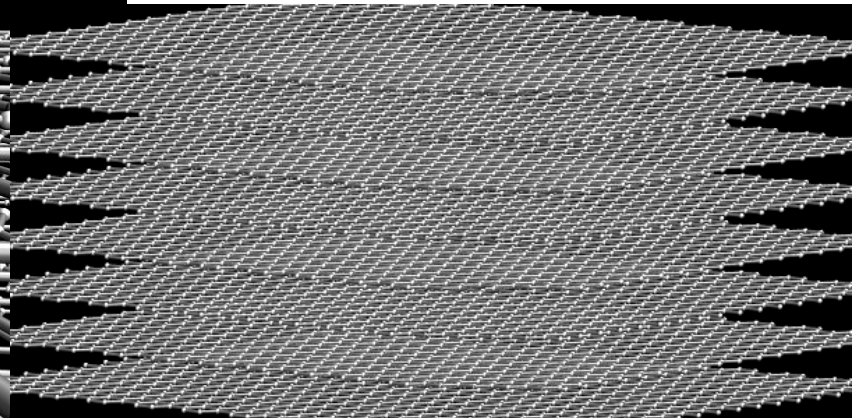
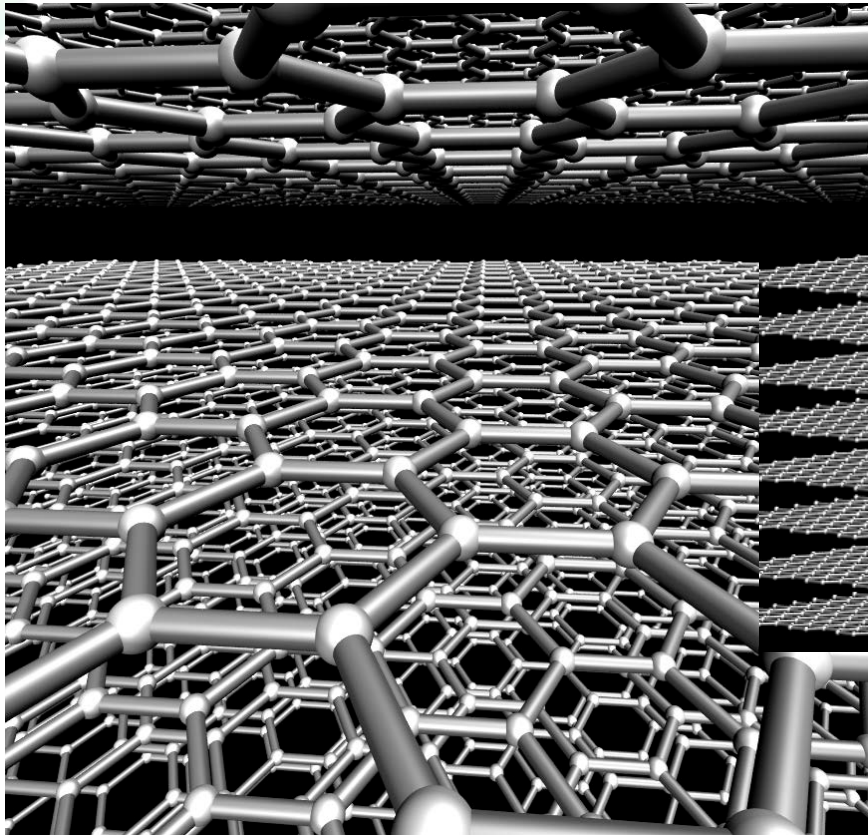
- Grafit och diamant är kända sedan urminnes tider
  - De är de två fasta jämvikstillståndena i fasdiagrammet för C



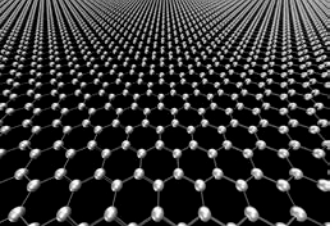


# Strukturen i grafit

- Grafits kristallstruktur är känd sedan början av 1900-talet
  - Sp<sup>2</sup>-bundet kol i lager på varandra



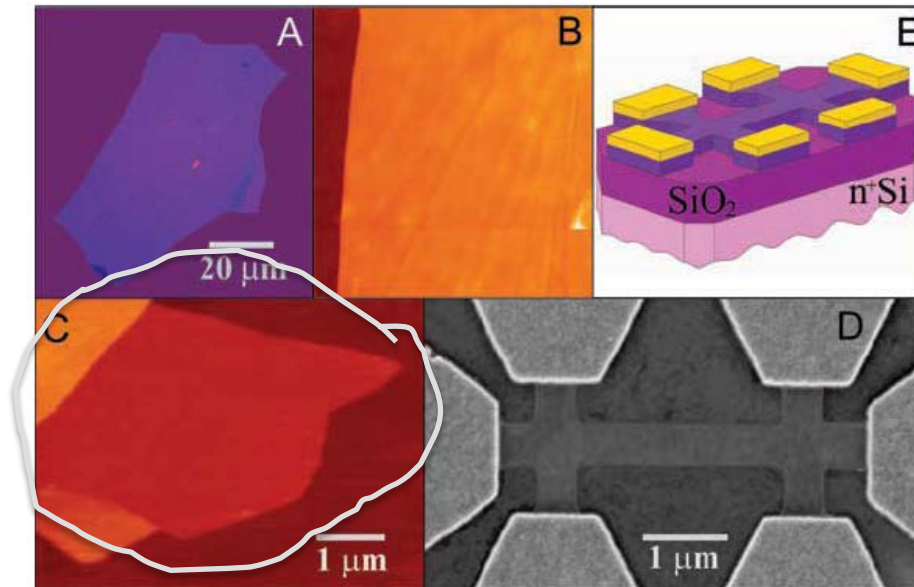


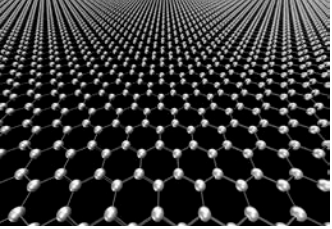


# Grafen (grafin)

- Att enskilda grafitlager existerar var alltså känt sedan mycket länge!
- Men få människor hade på allvar tänkt att isolera dessa lager
- De första som lyckades var Andre Geim och Konstatin Novoselov år 2004

[K. S. Novoselov, *Science* 306 (2004) 666;  
A. K. Geim *Science* **324**, 1530-1534 (2009) m.m.]





# Tillverkningsmetoden

- Den ursprungliga tillverkningsmetoden var förbluffande:

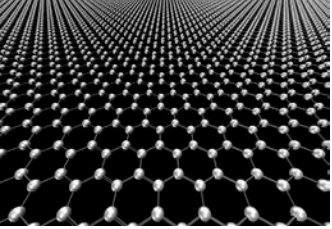
## Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,<sup>1</sup> A. K. Geim,<sup>1\*</sup> S. V. Morozov,<sup>2</sup> D. Jiang,<sup>1</sup>  
Y. Zhang,<sup>1</sup> S. V. Dubonos,<sup>2</sup> I. V. Grigorieva,<sup>1</sup> A. A. Firsov<sup>2</sup>

Our graphene films were prepared by mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite (15). This approach was found to be highly reliable and allowed us to prepare FLG films up to 10  $\mu\text{m}$  in size. Thicker films

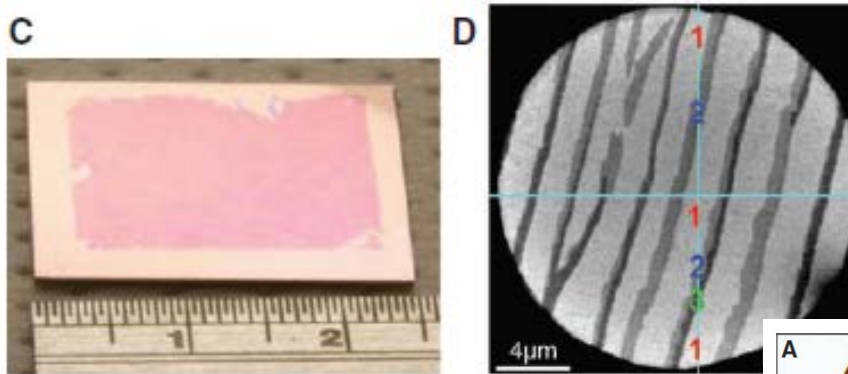
We used commercially available HOPG of grades ZYH ([www.ntmdt.ru](http://www.ntmdt.ru)) and HOPG-1 ([www.2spi.com](http://www.2spi.com)) with  $\mu > 100,000 \text{ cm}^2/\text{V}\cdot\text{s}$  at 4K. Using dry etching in oxygen plasma (S1), we first prepared 5  $\mu\text{m}$ -deep mesas on top of the platelets (mesas were squares of various sizes from 20  $\mu\text{m}$  to 2 mm). The structured surface was then pressed against a 1- $\mu\text{m}$ -thick layer of a fresh wet photoresist spun over a glass substrate. After baking, the mesas became attached to the photoresist layer, which allowed us to cleave them off the rest of the HOPG sample. Then, using scotch tape we started repeatedly peeling flakes of graphite off the mesas. Thin flakes left in the photoresist were released in acetone. When a Si wafer was dipped in the solution and then washed in plenty of water and propanol, some flakes became captured on the wafer's surface (as a substrate, we used  $n^+$ -doped Si with a  $\text{SiO}_2$  layer on top; in order to avoid accidental damage - especially during plasma etching - we chose to use relatively thick  $\text{SiO}_2$  with  $t = 300\text{nm}$ ). After this, we used ultrasound cleaning in propanol, which removed mostly thick flakes. Thin flakes ( $d < 10 \text{ nm}$ ) were found to attach strongly to  $\text{SiO}_2$ , presumably due to van der Waals and/or capillary forces.

To select from the resulting films only those that are just a few graphene layers thick, we used a combination of optical, electron-beam and atomic-force microscopy as described below.



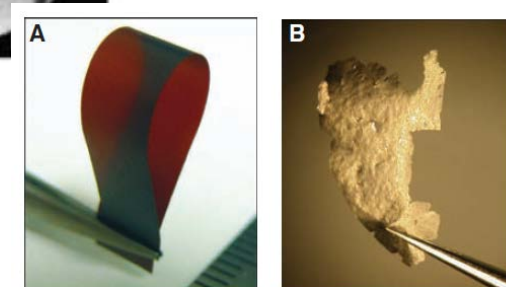
# Grafens egenskaper

- Ett idealt 2D-ledande system; mycket exotiska ledningsegenskaper ("massless Dirac fermions")
- Mycket hållbart mekanisk, oxideras inte i luft
- Numera kan grafen tillverkas på många olika sätt, t.ex. genom tillväxt på Ni

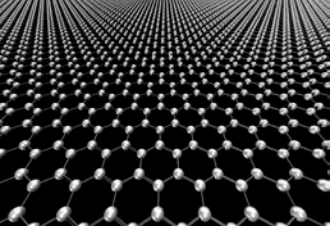


[A. K. Geim *Science* **324**,  
1530-1534 (2009)]

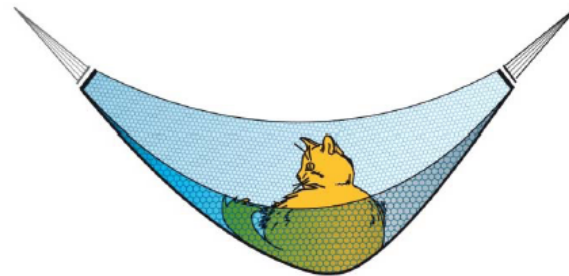
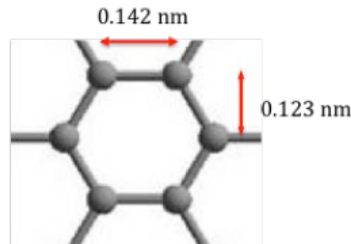
- Grafen-papper kan göras av grafenoxid



**Fig. 3.** Graphene derivatives. (A) Graphene oxide laminate is tough, flexible, transparent, and insulating (6). (B) Paper made in the same way as (A) but starting from graphene suspension (5) is porous, fragile, opaque, and metallic. [Courtesy of R. Nair, University of Manchester]



# Grafen är otrolig starkt!



## ***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  $0.77 \text{ mg}$ .

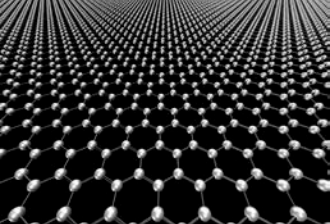
## ***Strength of graphene***

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.

[[http://static.nobelprize.org/nobel\\_prizes/physics/laureates/2010/sciback\\_phy\\_10.pdf](http://static.nobelprize.org/nobel_prizes/physics/laureates/2010/sciback_phy_10.pdf)]

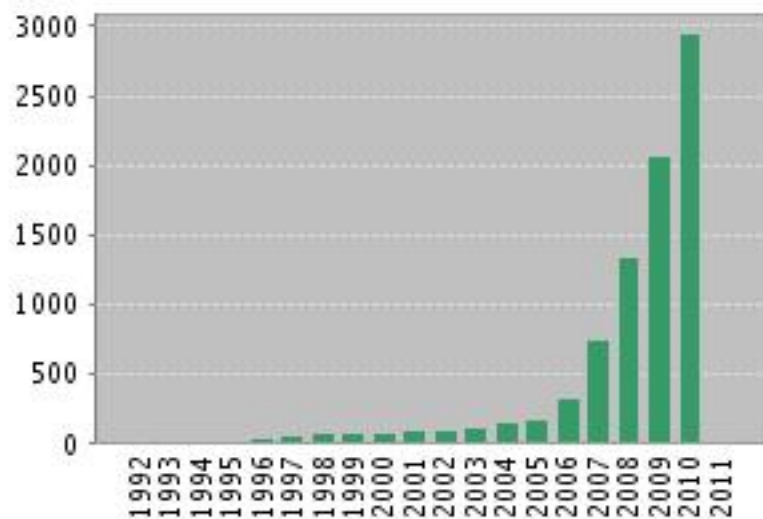




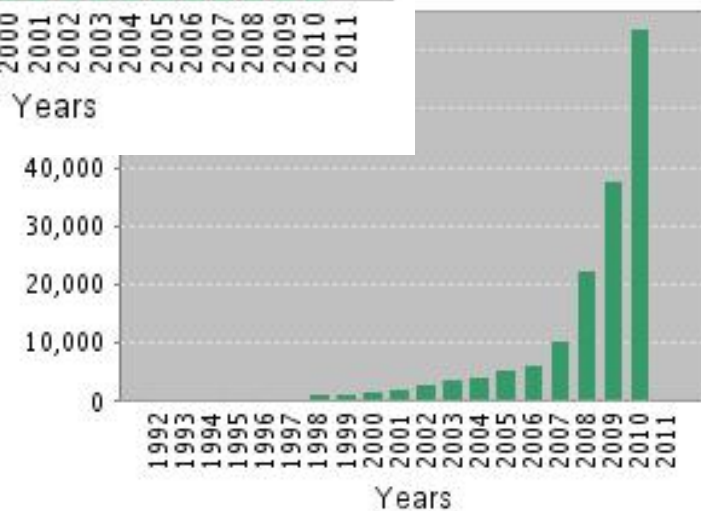
# Tillväxten av grafenforskning

- Sedan 2004 har grafenforskningen exploderat!

## Published Items in Each Year



## ach Year



Results found: 8,579

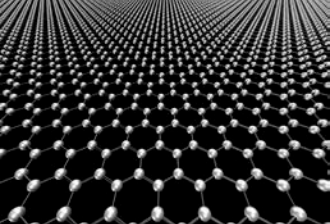
Sum of the Times Cited [?]: 165,737

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Average Citations per Item [?]: 19.32

h-index [?]: 160



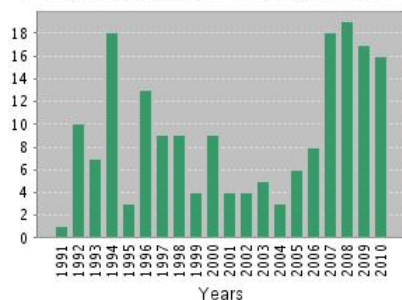
# Publikationer

## ■ Author search: Geim A\*

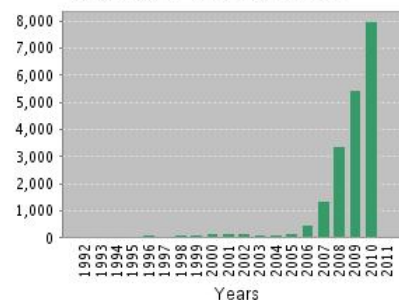
**Citation Report** Author=(geim a\*)  
Timespan=All Years. Databases=SCI-EXPANDED, SSCI, A&HCI.

This report reflects citations to source items indexed within Web of Science. Perform a Cited Reference Search to include citations to items not indexed within Web of Science.

**Published Items in Each Year**



**Citations in Each Year**



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Sum of the Times Cited [?]: 20,255

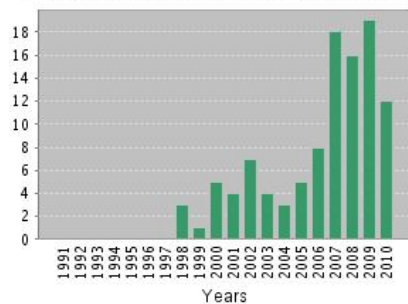
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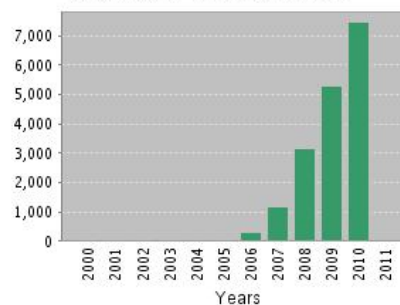
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## ■ Author search: Novoselov K\*

**Published Items in Each Year**



**Citations in Each Year**



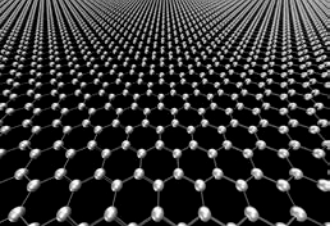
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Sum of the Times Cited [?]: 17,634

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Average Citations per Item [?]: 166.36

h-index [?]: 37



# Nobelpriset

- Allt detta gav Novoselov och Geim Nobelpriset 2010



The Nobel Prize in Physics 2010  
Andre Geim, Konstantin Novoselov

The Nobel Prize in Physics 2010

Nobel Prize Award Ceremony

Andre Geim

Konstantin Novoselov



Photo: Sergeom, Wikimedia Commons

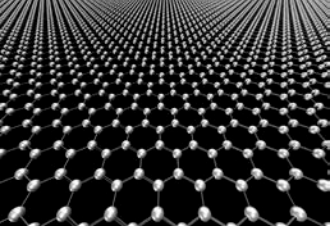
Andre Geim



Photo: University of Manchester, UK

Konstantin Novoselov

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*



# Andre Geim

## Biography

[[edit](#)]

Andre Geim was born to Konstantin Alekseyevich Geim and Nina Nikolayevna Bayer on October 1, 1958. Both his parents were [Russian German](#) engineers.<sup>[1]</sup> Geim has stated, "My mother's grandmother was Jewish. I suffered from [anti-Semitism](#) in Russia because my name sounds Jewish".<sup>[2]</sup> Geim has one brother, Vladislav. In 1965, the family moved to [Nalchik](#),<sup>[3]</sup> where he studied at an English-language high school.<sup>[3]</sup> After graduation, he applied to the [Moscow Engineering Physics Institute](#).<sup>[4]</sup> He took the entrance exams twice, but was not accepted.<sup>[3][5]</sup> He then applied to the [Moscow Institute of Physics and Technology](#) (MIPT), where he was accepted. He said the students had to work extremely hard: "The pressure to work and to study was so intense that it was not a rare thing for people to break and leave, and some of them ended up with everything from schizophrenia to depression to suicide." He received an MSc in 1982, and in 1987 obtained a PhD in [metal physics](#) from the [Institute of Solid State Physics](#) (ISSP) at the [Russian Academy of Sciences](#) (RAS) in [Chernogolovka](#).<sup>[6][7]</sup> He said that at the time he would not have chosen to study [solid-state physics](#), preferring particle physics or astrophysics, but is now happy with his choice.<sup>[6]</sup>

## Academic career

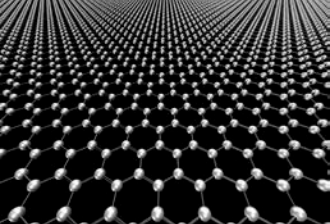
[[edit](#)]

After earning his PhD, Geim worked as a research scientist at the [Institute for Microelectronics Technology](#) (IMT) at RAS, and from 1990 as a post-doctoral fellow at the universities of [Nottingham](#) (twice), [Bath](#), and [Copenhagen](#). He said that while at Nottingham he could spend his time on research rather than have to deal with politics, and determined to leave Russia.<sup>[8]</sup>

He obtained his first tenured position in 1994, when he was appointed associate professor at [Radboud University Nijmegen](#), where he did work on [mesoscopic superconductivity](#). He later gained Dutch citizenship. One of his doctoral students at Nijmegen was [Konstantin Novoselov](#) to become his main research partner.

In 2001 he became a professor of physics at the [University of Manchester](#), and was appointed director of the Manchester Centre for Mesoscopic Nanotechnology in 2002, and [Langworthy Professor](#) in 2007.<sup>[7]</sup> Geim's wife and his long-standing co-author, Irina Grigorieva, also moved to Manchester. Later they were joined by Novoselov.<sup>[3]</sup> Since 2007 he has been an [EPSRC Senior Research Fellow](#).<sup>[7]</sup>





# Konstantin Novoselov

## Early life

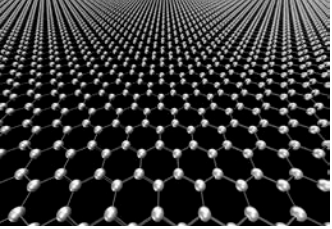
[[edit](#)]

Konstantin Novoselov was born in [Nizhny Tagil](#), [Soviet Union](#), in 1974 in a Russian family.<sup>[6]</sup> He received a Diploma from the [Moscow Institute of Physics and Technology](#), and undertook his PhD studies at the [University of Nijmegen](#) in the Netherlands before moving to the [University of Manchester](#) in the United Kingdom with his [doctoral advisor Andre Geim](#) in 2001. He now holds both Russian and British citizenship.<sup>[6]</sup>

## Career

[[edit](#)]

Novoselov has published more than 60 [peer-reviewed](#) research papers, on topics like mesoscopic [superconductivity](#) ([Hall magnetometry](#)),<sup>[7]</sup> sub-atomic movements of [magnetic domain walls](#),<sup>[8]</sup> the invention of [gecko tape](#),<sup>[9]</sup> and [graphene](#).<sup>[10]</sup>



# Förhållande till andra kolnanostrukturer

- De övriga kol-nanostrukturerna kan konceptuellt förstås på basen av grafen
  - Men verklig tillväxt något helt annat!

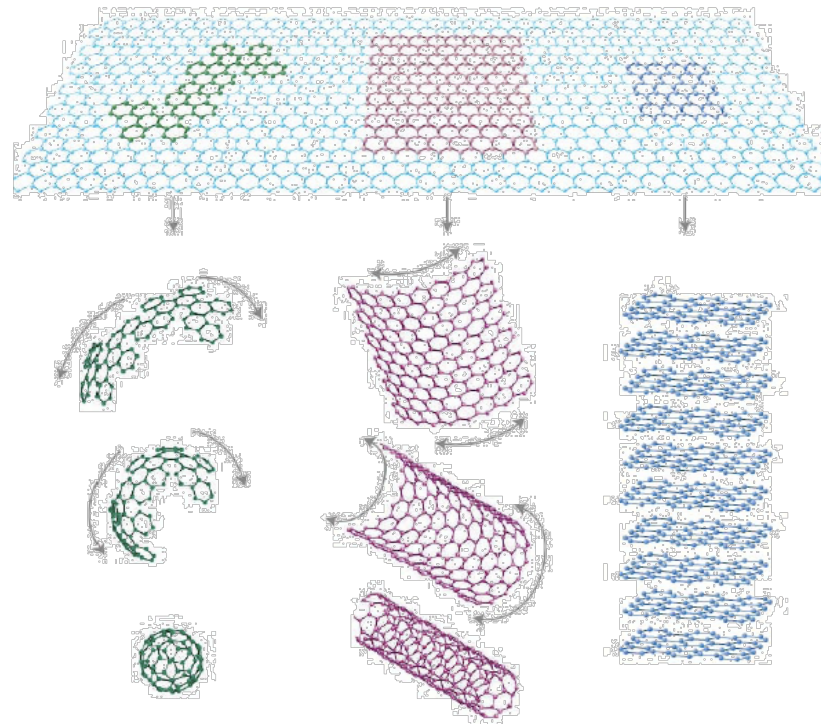
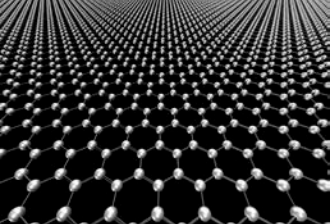


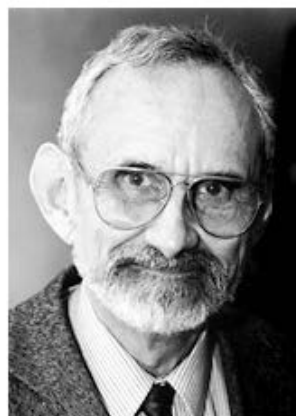
Figure 1. C60 fullerene molecules, carbon nanotubes, and graphite can all be thought of as being formed from graphene sheets, *i.e.* single layers of carbon atoms arranged in a honeycomb lattice.<sup>12</sup>



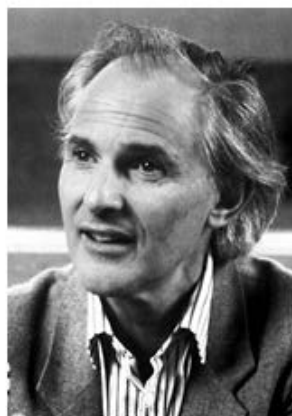
# Fullerener

- Fulleren-molekylen  $C_{60}$  hittades redan 1985 av Kroto, Smalley & co.
- Runda små kolmolekyler
- Gav Nobelpriset i kemi 1996:

<b>The Nobel Prize in Chemistry 1996</b>
Nobel Prize Award Ceremony
Robert F. Curl Jr.
Sir Harold Kroto
Richard E. Smalley



Robert F. Curl Jr.

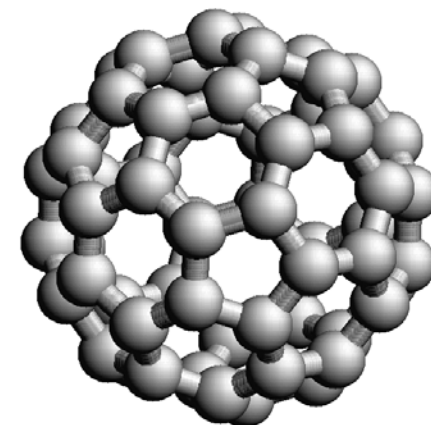


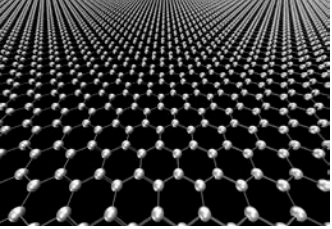
Sir Harold W. Kroto



Richard E. Smalley

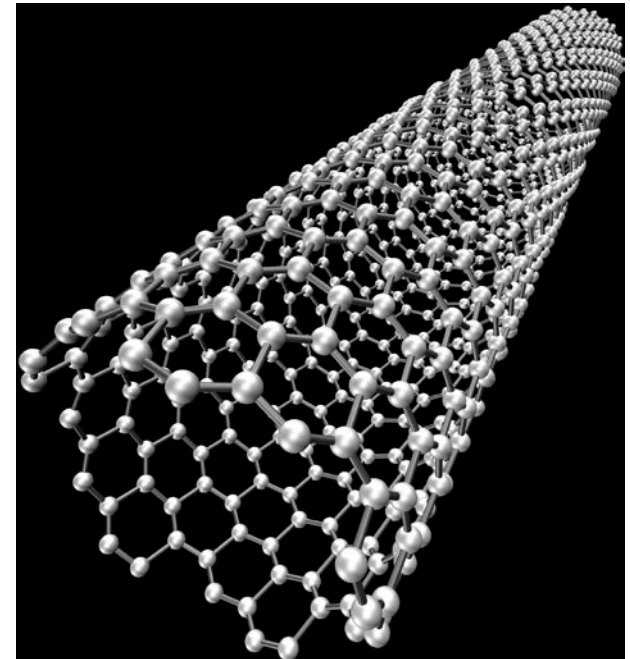
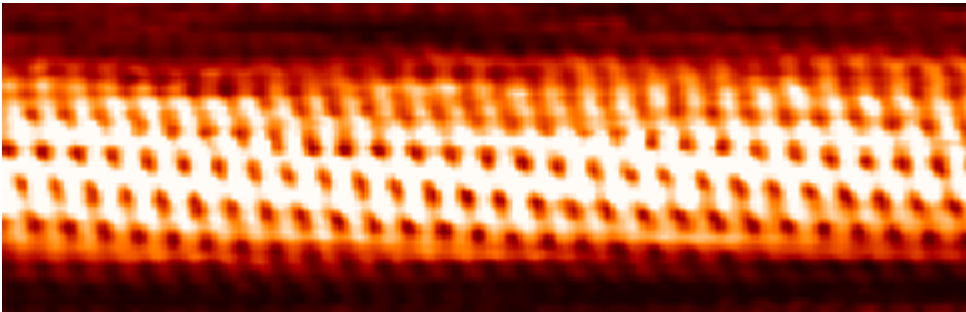
The Nobel Prize in Chemistry 1996 was awarded jointly to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley "for their discovery of fullerenes".



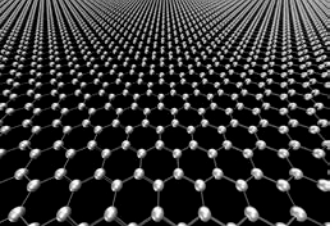


# Kolnanorör – en historisk orättvisa?

- Kolnanorör upptäcktes 1991 av Sumio lijima
- De har sedan dess forskats i en massa, och har långt fler publikationer än grafen och redan en massa praktiska tillämpningar
- Varför fick inte lijima priset??





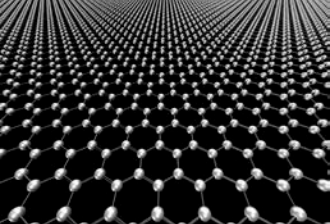


## Kanske p.g.a. följande:

- Oftast sägs det att kolnanorör hittades av Sumio Iijima år 1991.
- Men men:
  - Ryska forskare hittade dem antagligen redan på 1960-talet
  - R. Bacon, National Carbon Comp., Parma, Ohio producerade antagligen dem redan 1960.
  - M. Endo, Japan, producerade dem och publicerade resultaten år 1977
  - P. Wiles, University of Canterbury, Nya Seeland producerade dem år 1979



- ***Nobelkommittén ville inte befatta sig med denna härva??***



# Leviterande grodor!

- Men Andre Geim var redan berömd före grafen!
- Han vann år 2000 anti-Nobelpriset för sitt arbete med att levitera grodor!

## PHYSICS

**Andre Geim** of the University of Nijmegen (the Netherlands) and **Sir Michael Berry** of Bristol University (UK), for using magnets to levitate a frog. [REFERENCE: "Of Flying Frogs and Levitrons" by M.V. Berry and A.K. Geim, European Journal of Physics, v. 18, 1997, p. 307-13.]

## Of flying frogs and levitrons

M V Berry<sup>†</sup> and A K Geim<sup>‡</sup>

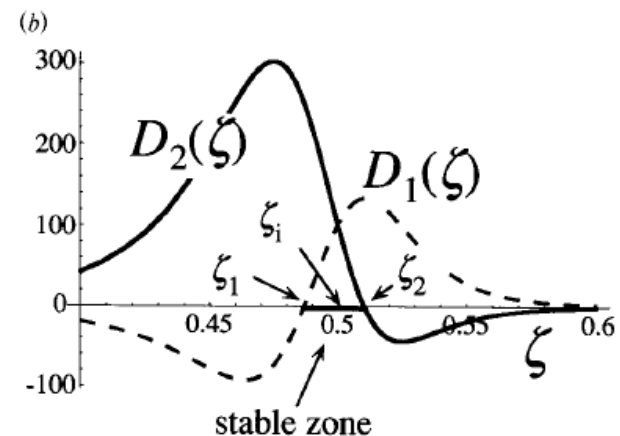
<sup>†</sup> H H Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, UK

<sup>‡</sup> High Field Magnet Laboratory, Department of Physics, University of Nijmegen, Toemooiveld, 6525 ED Nijmegen, The Netherlands

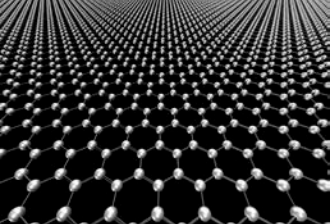
Received 4 June 1997

**Abstract.** Diamagnetic objects are repelled by magnetic fields. If the fields are strong enough, this repulsion can balance gravity, and objects levitated in this way can be held in stable equilibrium, apparently violating Earnshaw's theorem. In fact Earnshaw's theorem does not apply to induced magnetism, and it is possible for the total energy (gravitational + magnetic) to possess a minimum. General stability conditions are derived, and it is shown that stable

**Samenvatting.** Magnetische velden stoten diamagnetische voorwerpen af. Zulke velden kunnen zo sterk zijn dat zij de zwaartekracht opheffen. Het is op deze wijze mogelijk zulke voorwerpen te laten zweven. Dit vormt een stabiel evenwicht, wat in tegenspraak schijnt te zijn met Earnshaw's Theorema. Echter Earnshaw's Theorema is niet langer geldig als het magnetisme veld geïnduceerd is. De totale energie (bevattende bijdragen van het magnetisme en de



**Figure 2.** (a) Field on the axis inside a solenoid with  $\delta = 2a/L = 0.1$ ; (b) the discriminants  $D_1(\xi)$  and  $D_2(\xi)$  defined by (16), and the stable zone where both are positive.



## Leviterande grodor!

Geim: "Playful attitude to physics"



<http://www.youtube.com/watch?v=A1vyB-O5i6E>