Random Walk to Graphene

“STORY BEHIND”

timeline: from 1987 to *Science* 2004
starting with stories irrelevant to graphene
but relevant to a bigger picture

PhD 1987

"Investigation of mechanisms of transport relaxation in metals by a helicon resonance method"

ДИПЛОМ
КАНДИДАТА НАУК

ФМ № 030224

Москва 6 января 1988 г.

Решением
Совета при Институте физики твердого тела АН СССР
от 30 июня 1987 г. (протокол № 9)
Гейму Андрею Константиновичу
ПРИСУЖДЕНА УЧЕНАЯ СТЕПЕНЬ
КАНДИДАТА
ФИЗИКО-МАТЕМАТИЧЕСКИХ НАУК

Председатель совета
Ученый секретарь совета

as exciting as it sounds

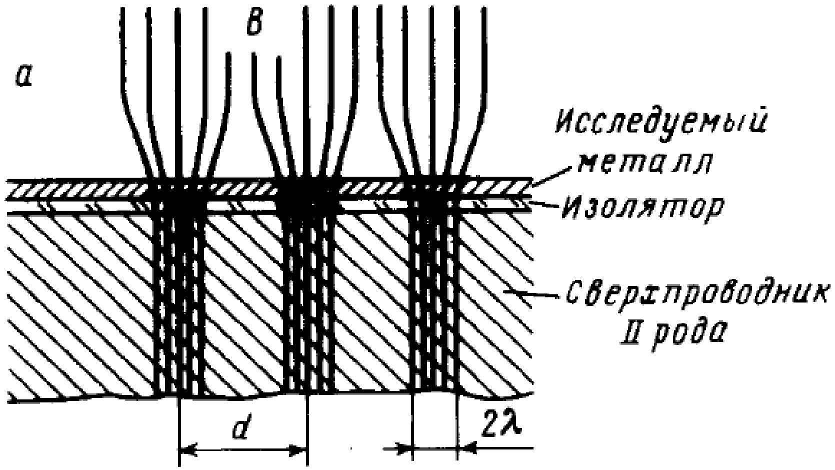
message I took away:

NEVER TORTURE STUDENTS WITH BORING/DEAD PROJECTS !

SWEET TASTE OF FREEDOM

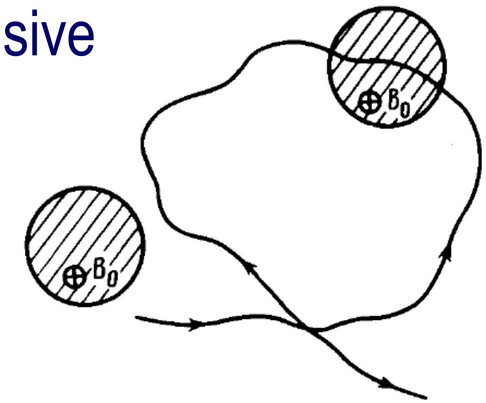
staff scientist in Chernogolovka: 1988-1990

something new but still possible with available Soviet facilities

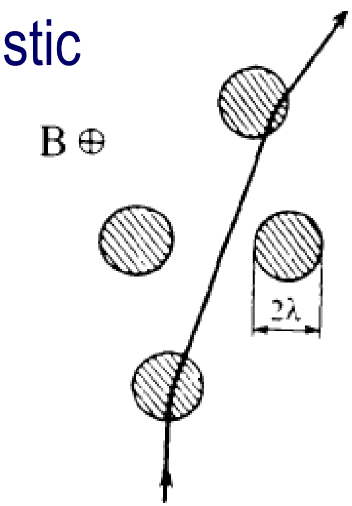


magnetic field inhomogeneous on a submicron scale

diffusive



ballistic



experience I took away:

NEW EXPERIMENTAL SYSTEM IS BETTER THAN A NEW PHENOMENON !

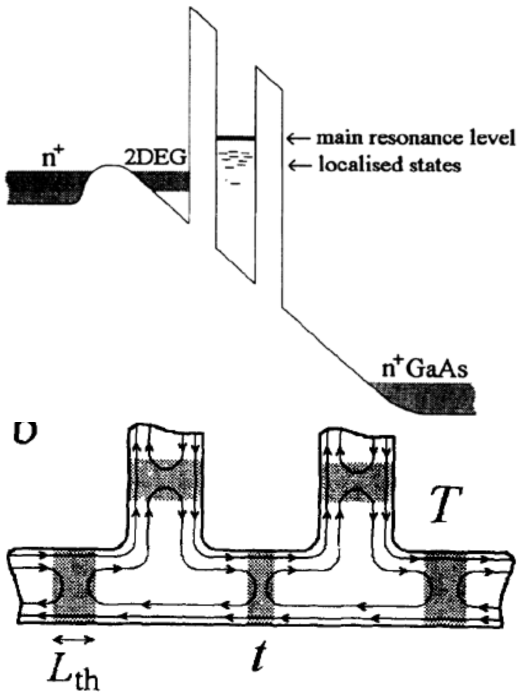
Geim, *JETP Lett.* 1989
Geim, Sergey Dubonos *et al* *JETP Lett.* 1990
later, two *PRL* 1991, 1994

MOVING YEARS

postdocs in Nottingham x2, Bath & Copenhagen: 1990-1994

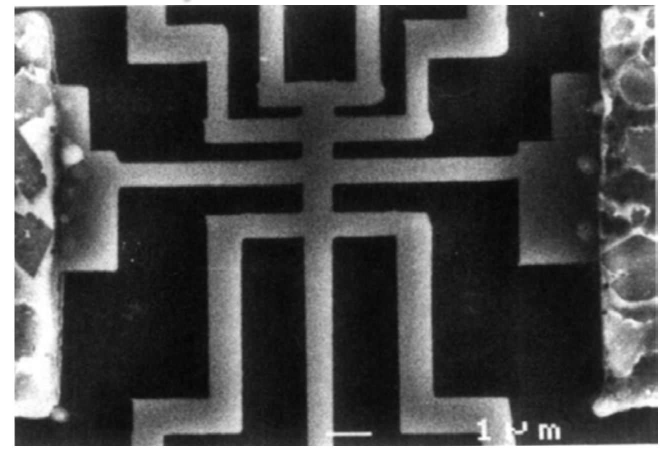
age =32
h-index ~1

SEMICONDUCTOR PHYSICS



GaAlAs heterostructures
universal conductance fluctuations
resonant tunnelling phenomena
quantum point contacts
quantum Hall effect
2DEG in periodic potentials

my first 6-month visit



submicron GaAs wires from a drawer

Geim, Laurence Eaves, Peter Main *et al*
Phys. Rev. Lett. 1991
Phys. Rev. Lett. 1992

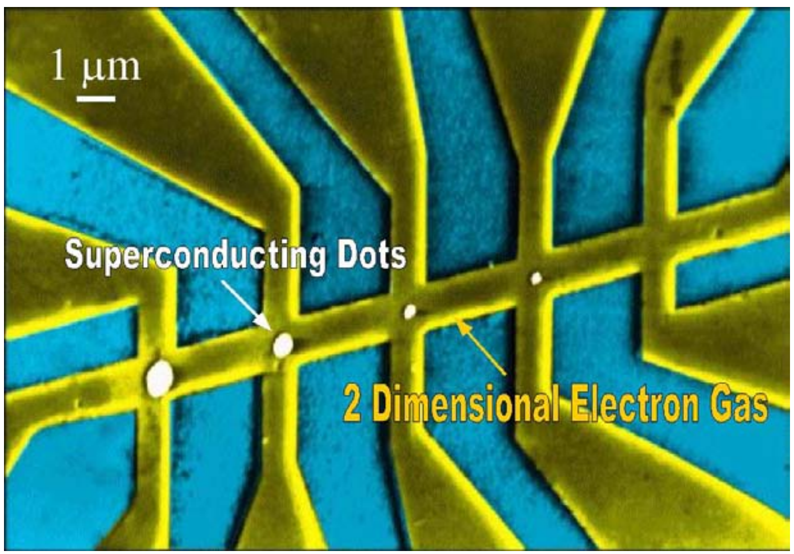
experience to tease colleagues:
"NO SUCH THING
AS BAD SAMPLES,
ONLY BAD POSTDOCS ☺"

GOING DUTCH

associate professor in Nijmegen: 1994-2000

FINDING RESEARCH NICHE: possible but somewhat different

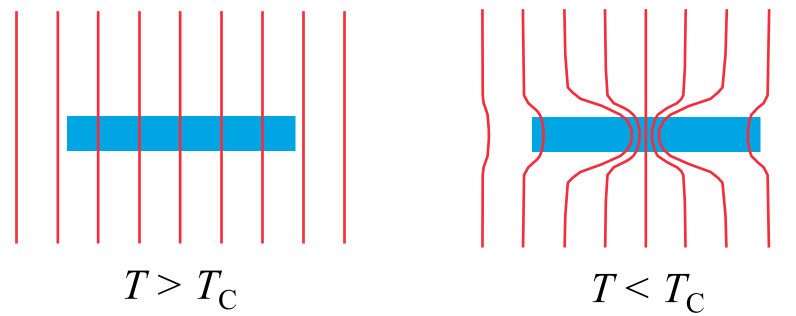
micron-sized Hall probes to investigate superconductors, ferromagnetics, etc



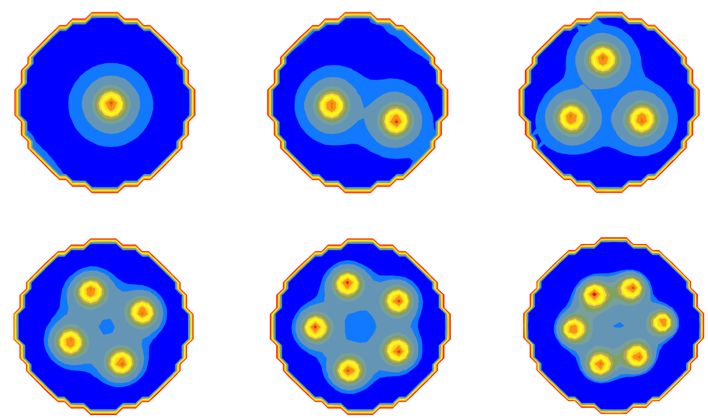
structures from Nottingham
lithography in Russia: Sergey Dubonos
measurements in Nijmegen

MESOSCOPIC SUPERCONDUCTIVITY

paramagnetic Meissner effect



fractional flux vortices & vortex shells



writing up with Irina Grigorieva:

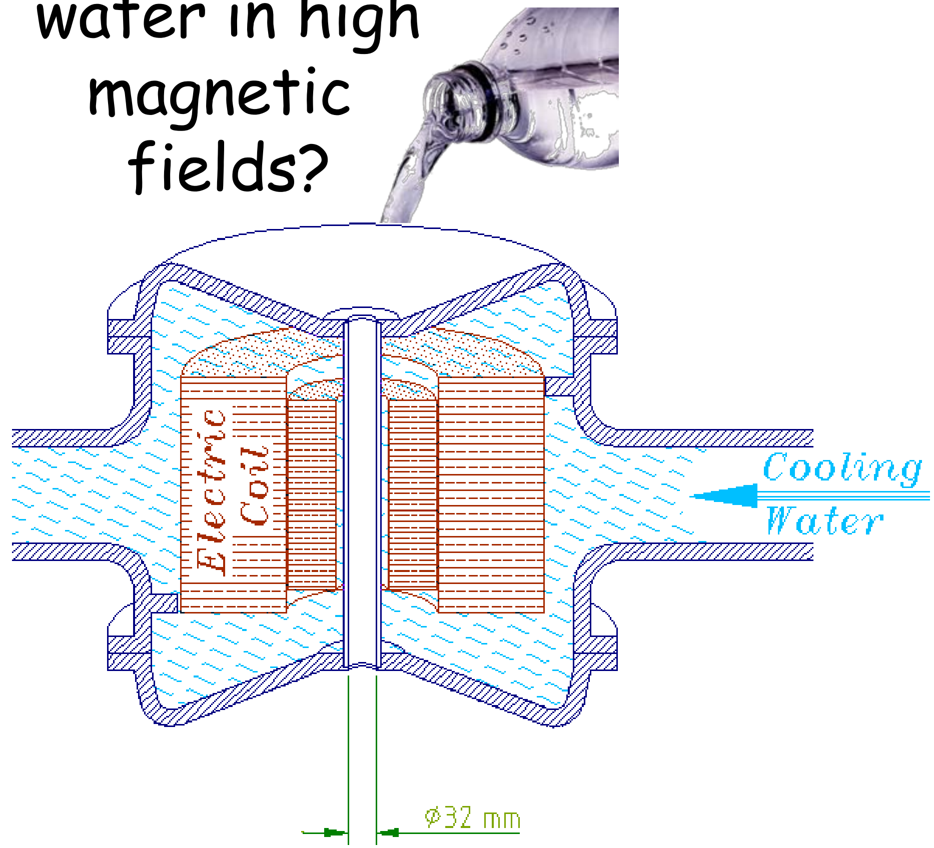
Nature **390**, 259 (1997); *Nature* **396**, 144 (1998); *Nature* **407**, 55 (2000); *PRL* **79**, 4653 (1997); *PRL* **85**, 1528 (2000)

"FRIDAY NIGHT EXPERIMENTS"

starting 1997

magnetic water descaler

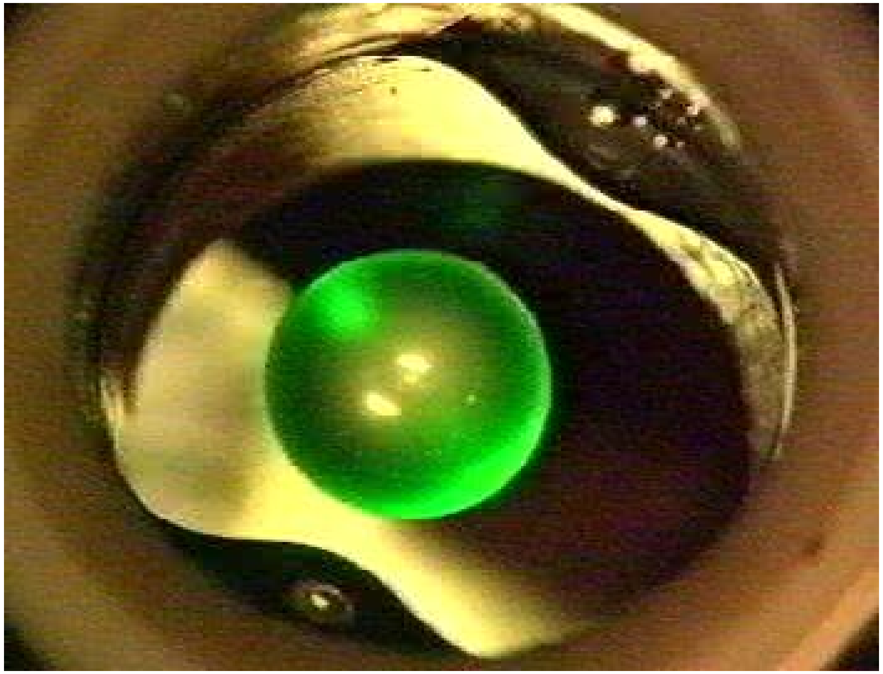
water in high magnetic fields?



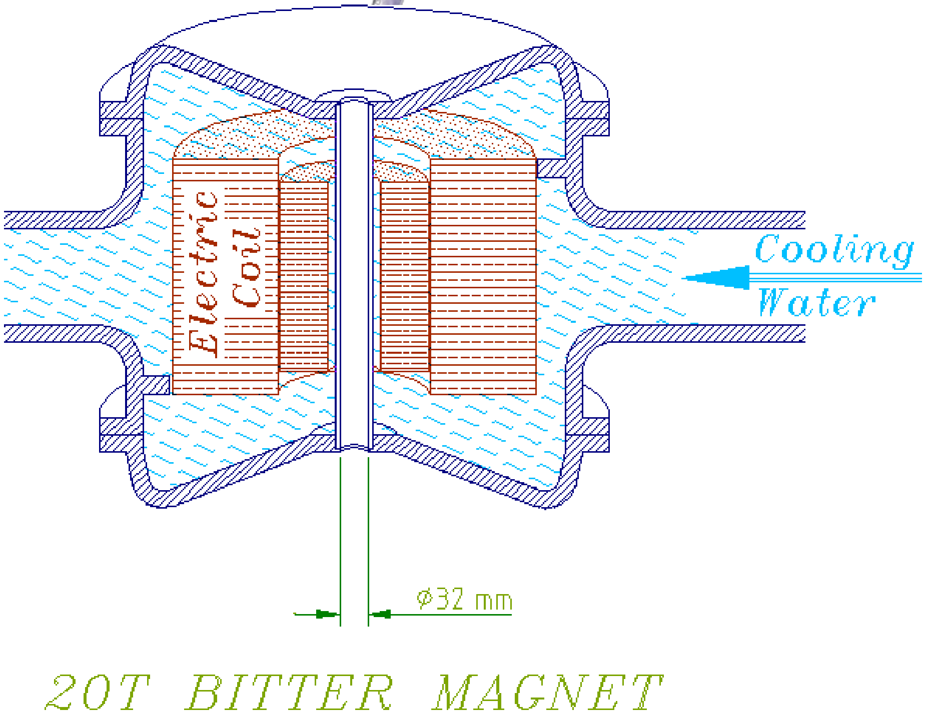
20T BITTER MAGNET

ancient magnets:
consume a lot of energy
require extra cryostats

A BIT OF LEVITY



water in high magnetic fields



NEEDS EMPHASIS

Levitation of organic materials

SIR—We have succeeded in levitating at room temperature 'nonmagnetic' materials by means of a strong inhomogeneous static magnetic field. Such materials are in fact weakly diamagnetic and, when subjected to a magnetic field gradient, tend to be driven from regions of high field to those of lower field. When the resulting force is upwards and stronger than gravity, levitation occurs.

The critical criteria for levitation are the intrinsic magnetic property of the diamagnetic material (the specific magnetic susceptibility) and G, the gradient of the square of the magnetic field. For completeness, we also report B, the field at which the coils were driven to obtain such a gradient.

In the 5-cm cylindrical room-temperature bore of the hybrid magnet of the Service National des Champs Intenses (Grenoble), we have levitated various diamagnetic solids and liquids. Pure samples of bismuth and antimony were levitated with $G_{Bi} = 729\ T^2\ m^{-1}$, $B_{Bi} = 15.87$ T and $G_{Sb} = 1{,}208\ T^2\ m^{-1}$, $B_{Sb} = 18.75$ T, respectively, values in very good agreement with calculations based on magnetic susceptibility data (R. C. Weast, *Handbook of Chemistry and Physics* 1972–73). Pieces of wood and plastic were levitated with $1{,}648\ T^2\ m^{-1} < G_w < 1{,}753\ T^2\ m^{-1}$, $21\ T < B_w < 21.5$ T and $G_p = 1{,}923\ T^2\ m^{-1}$, $B_p = 22.28$ T, respectively. Water, ethanol and acetone were levitated with $2{,}961\ T^2\ m^{-1} < G_w < 3{,}097\ T^2\ m^{-1}$, $26.5 < B_w < 27$ T, $1{,}445\ T^2\ m^{-1} < G_e < 1{,}648\ T^2\ m^{-1}$, $20\ T < B_e < 21$ T and $1{,}862\ T^2\ m^{-1} < G_a < 2{,}086\ T^2\ m^{-1}$, $22\ T < B_a < 23$ T, respectively. Values for the liquids were higher than expected and may result from wetting effects in the apparatus.

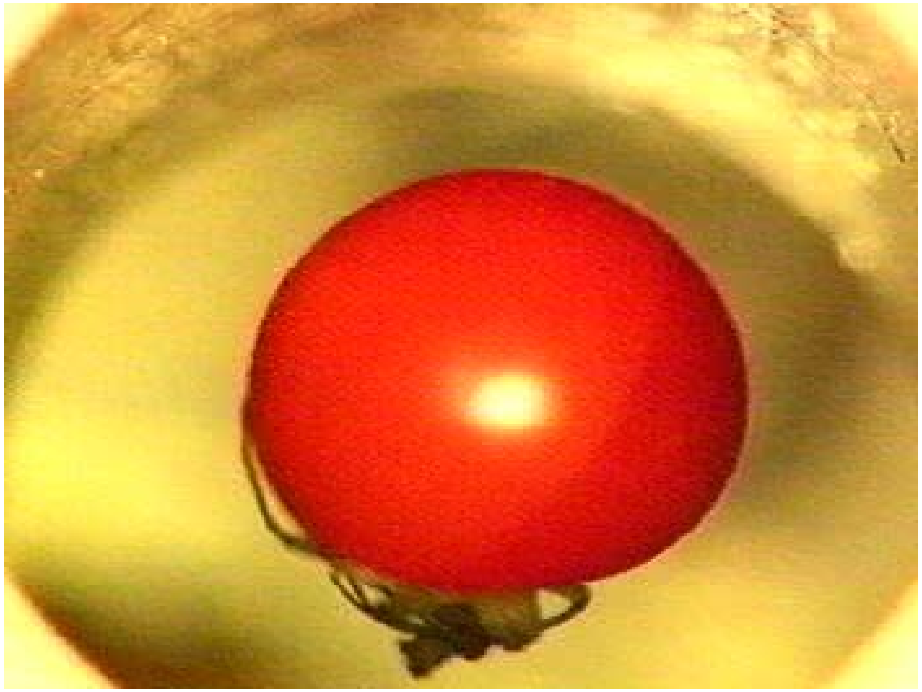
We have studied the levitation of graphite in a lower field magnet with a much larger bore ($G_g = 140\ T^2\ m^{-1}$ and $B_g = 5.25$ T). We have confirmed that the levitation was very stable, without any contact with the magnet bore.

Our technique could be used to provide a contactless, microgravity environment for the elaboration of a wide range of materials. The case of organic materials is of great interest as they all have almost the same specific diamagnetic susceptibility, high enough to achieve levitation in superconducting magnets.

E. BEAUGNON
R. TOURNIER
CNRS, Centre de Recherule sur les Très Basses Températures, Laboratoire associé á l'université Joseph Fourier, 25 Ave des Martyrs, 38042 Grenoble Cedex, France

Nature 1991

KNOWLEDGE IS FUN

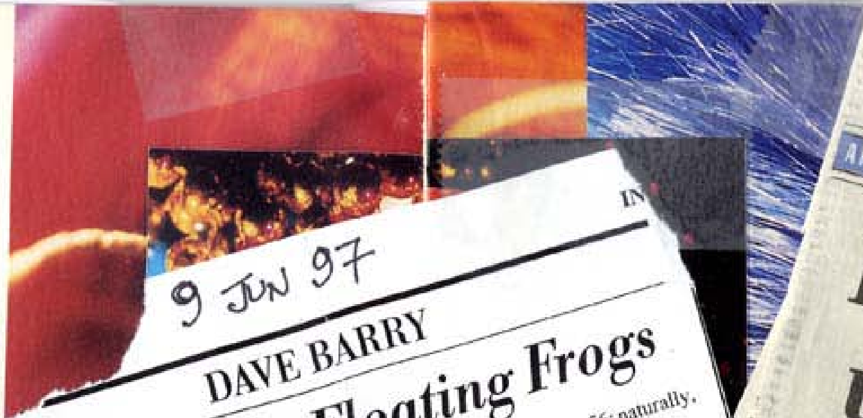


WOW! FACTOR

New Scientist, 26 July

And God said

...let there be levitating strawberries, flying frogs and humans that hover over Seattle. *Mark Buchanan* went forth in search of miracles



9 JUN 97

DAVE BARRY

Facts About Floating Frogs

MIAMI — Get ready to dance naked in the streets, because scientists have finally done something that humanity has long dreamed about, but most of us thought would never happen within our lifetimes.

That's right: They have levitated a frog.

I swear I am not making this up. According to an Associated Press article sent in by a number of alert readers, ... Dutch scientists "have suc- ... a frog in air." They ... magnetism, which, as ...

how many times 7 goes into 56; naturally, the child prefers the bed.

Think, parents, how much easier it would be if, at 6:30 A.M. on school mornings, you could simply press a button, thereby activating gigantic magnets under your child's bed that would cause the child to float upward, along with any frogs that happened to be in bed with the child. Then, instead of wasting your time yelling, "YOU'RE GOING TO BE LATE FO... SCHOOL!" you could waste your ... yelling, "STOP DRAWING ... THAT MARKING PEN O... CEILING!" So perhaps this ... od use for magnetic le...

APRIL 12, 1997

It's al... up in the air

Scientists magnetised by levitating frog

The Independent 12/04/97

Charles Arthur
Science Editor

Take one extremely powerful magnet, and one slightly ... prised but complia... one on to... wha...

project to build a magnet str... enough to levitat... 100 metr...

...t issue is your ... effects ... th... P...

sensation, though, being weightless. It's not a surface effect, like ... you ...

NEWS OF THE WORLD, October 5, 1997

INCREDIBLE!

Animal magnetism machi... frog float in thin ...

Gravity is leap-frogged by a magnet

By Aisling Irwin
Science Correspondent

A DUTCH frog may have become the first living creature to experience levitation. Physicists made it rise and hover in the air using a strong magnetic field. They repeated the procedure with a cheese sandwich.

The physicist...

The Guardian April 12, 1997

Frog floats throug...

Sue Quinn

HUMANS could soon ... ready for the ultimate ... lifting experience, ac... to scientists who h... frog levitate six f...

British and ... cists used ... netic fiel... force ... the ... w...

to ge... force ... oppos... ... bee...

LEVITY

GET READY TO dance naked in the streets, because scientists have done something that humanity has long dreamed about but that most of us thought would never happen. That's right: They levitated a frog. According to an Associated Press article, British ... have

floating in the air inside a magnetic cylinder."

I am not a trained scientist, but my reaction to that last statement is – and I quote – "Duh." Of course the frog "showed no signs of distress": It's a frog. Frogs are not known for showing emotions; they are limited to essentially one facial expression, mu... like Jean-Claude Van Damme. What did the ... entists expect the f... Hop arou...

PERCEPTION CHANGE

everything (and everybody) is magnetic;
ever present diamagnetism is NOT negligible

in many textbooks

messages to take away:

LOOK FOR
COMPETITIVE EDGE

even obsolete facilities
may offer some

sideline experience
of the IgNobel Prize:

DON'T TAKE
YOURSELF TOO SERIOUSLY

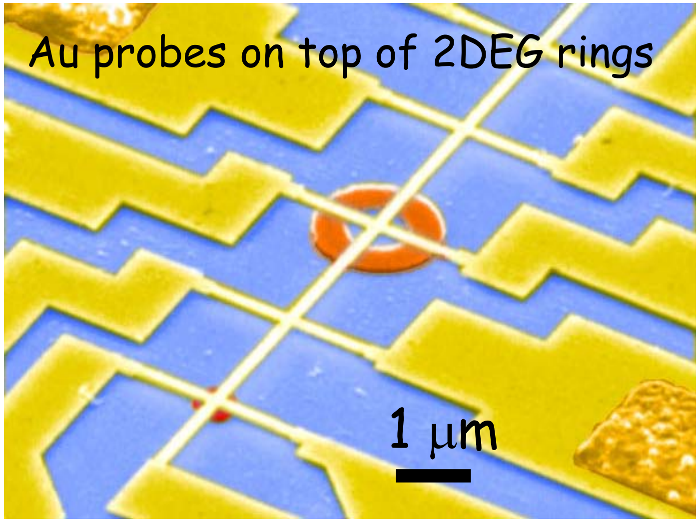
MANCUNIAN WAY

chair in Manchester: 2001 – present

empty lab; little start-up; no central microfabrication

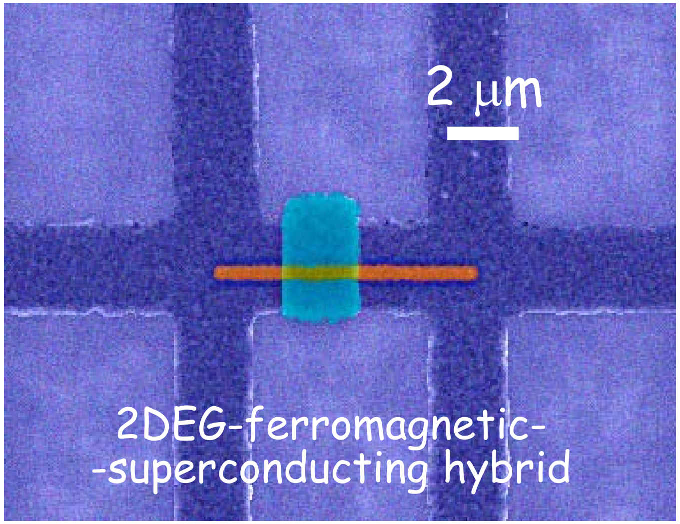
FIRST ESTABLISH YOURSELF & SET UP NEW FACILITIES

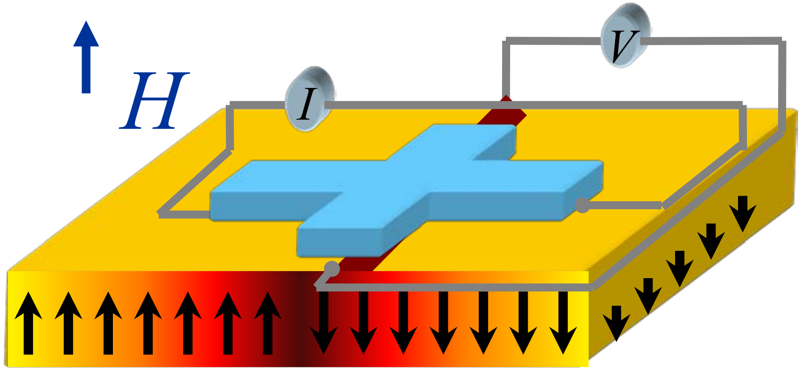
microfabrication still in Russia (Dubonos)



Kostya Novoselov *et al*, *Nature* **426**, 812 (2003)
Irina Grigorieva *et al*, *PRL* **92**, 237001 (2004)

by 2003: well-equipped lab and state-of-the-art microfabrication thanks to EPSRC & University

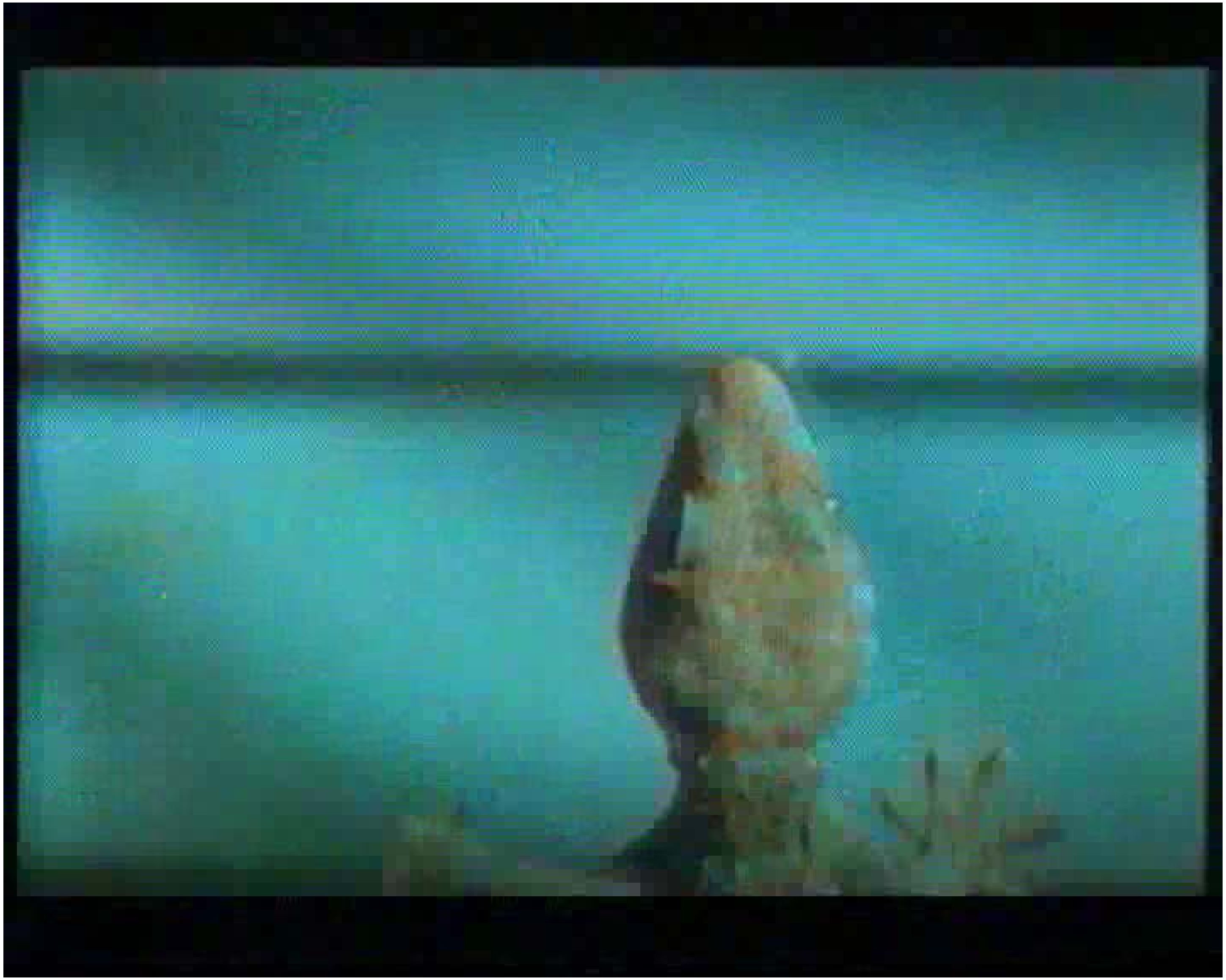




subatomic movements of domain walls

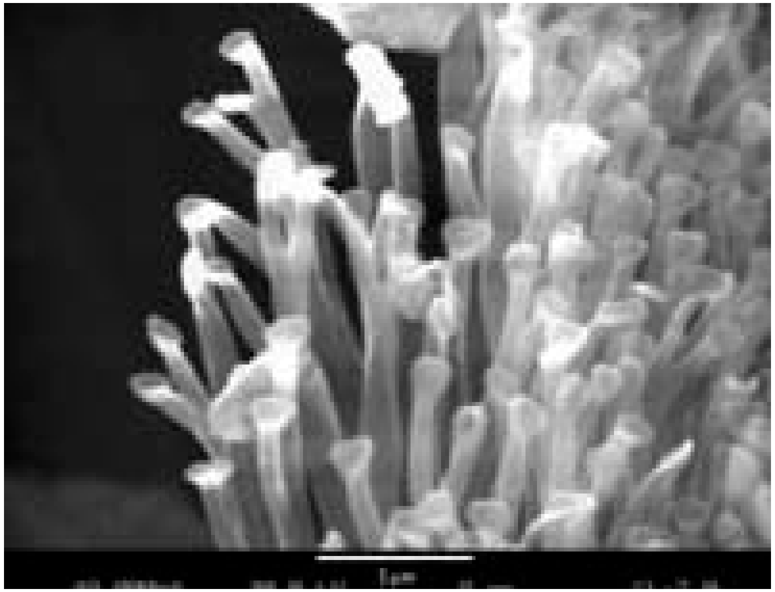
"FRIDAY NIGHTS" in MANCHESTER

HOW COMES THAT GECKO CAN CLIMB WALLS?



“FRIDAY NIGHTS” in MANCHESTER

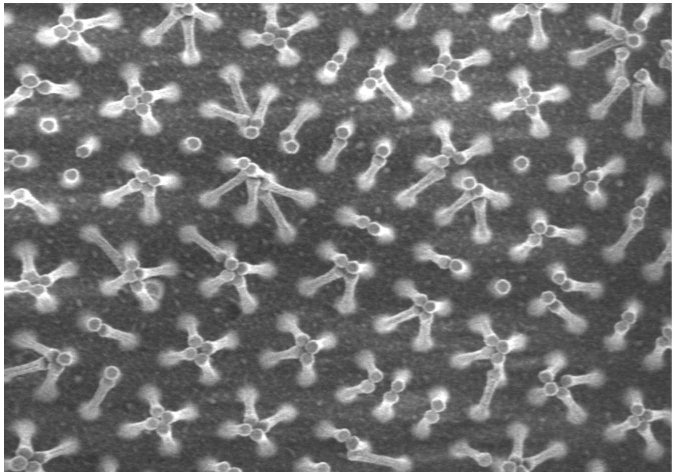
sticky feet:
geckos climb due to their hairy toes

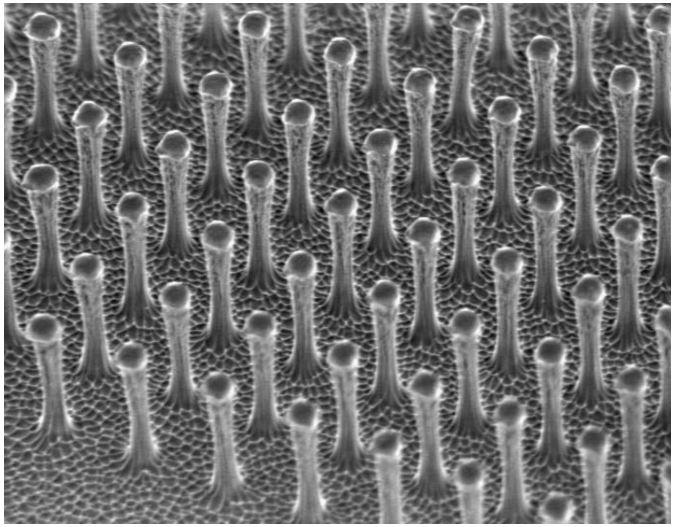


submicron size (!) - standard spatial scale in our work

GECKO TAPE

proof of concept:
biomimetic dry adhesive
based on "gecko principle"





PLACING EMPHASIS

Geim, Sergey Dubonos,
Irina Grigorieva, Kostya Novoselov *et al*
Nature Materials 2003

"FRIDAY NIGHT" FAILURES

magnetic water

3 different attempts – Sergey Morozov

permeability of high- T_c superconductor to oxygen

Jeroen Meessen in Nijmegen

… … …

high- T_c superconductivity in NiAs+FeSe alloys

Lamarches' samples (*EPL* 2000)

well before the discovery of pnictide superconductivity

detection of "heart beats" of individual yeast cells

(Irina Barbolina, Kostya Novoselov *et al APL* 2006)

… … …

experience I am still mulling over:

FAILURES ARE NOT AS OFTEN AS ONE CAN EXPECT

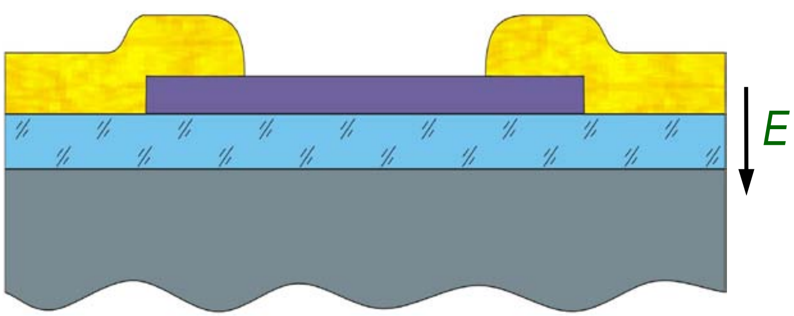
BRIEF HISTORY OF GRAPHENE

One Little Thought Cloud

metallic electronics

Schlesinger 2000
Lemanov & Kholkin 1994
Petrashov 1991
...
Bose (1906)
Mott (1902)

mostly, Bi
changes ~1%



change the number of electrons
-> change conductivity

electric breakdown ~1V/nm
max induced concentration $\approx 10^{14}$ cm^{-2}

single atomic layer of a metal $\approx 10^{15}$ cm^{-2}
rarely stable for thickness below 100 Å

One Little Thought Cloud

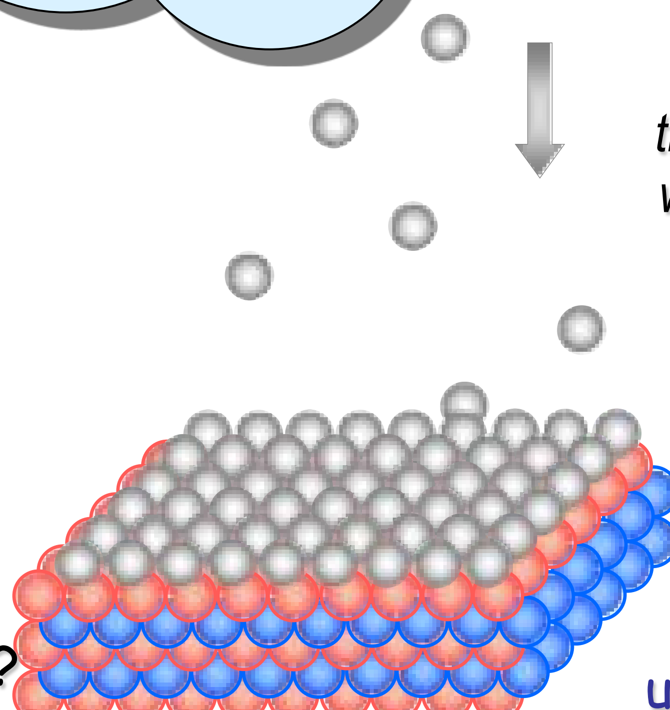
metallic electronics

Schlesinger 2000
Lemanov & Kholkin 1994
Petrashov 1991
...
Bose (1906)
Mott (1902)

MANY MANY DIFFERENT EPITAXIAL SYSTEMS

~few nm thick Al grown by MBE on top of GaAlAs from Nottingham

tinkering for >10 years with the following idea



WOULD IT BE STABLE, OR MELT AND OXIDIZE?

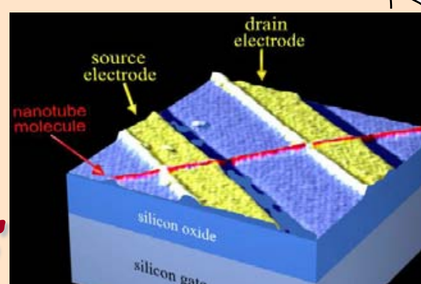
chemically remove the substrate
↓
ultra-thin monocrystal

Two More Little Clouds

metallic electronics

Schlesinger 2000
Lemanov & Kholkin 1994
Petrashov 1991
...
Bose (1906)
Mott (1902)

carbon nanotube transistors



Ijima, Ebbesen, McEuen
Dekker, Avouris

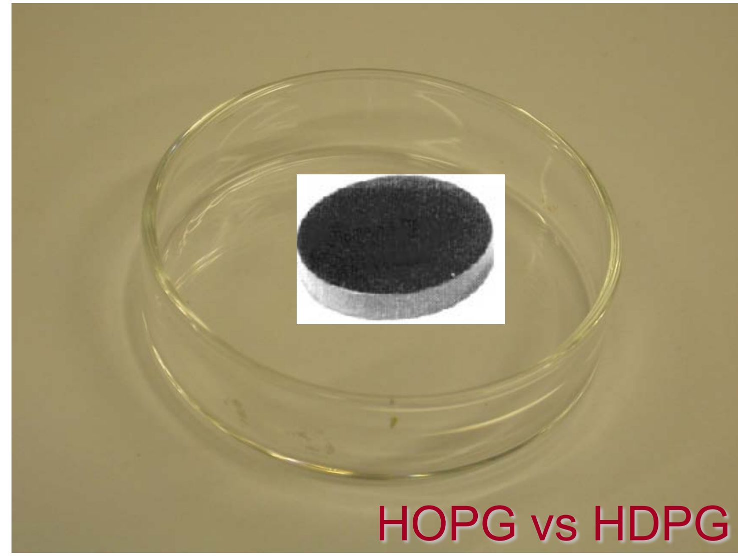
Dresselhauses' review 1981

little known about thin films of graphite

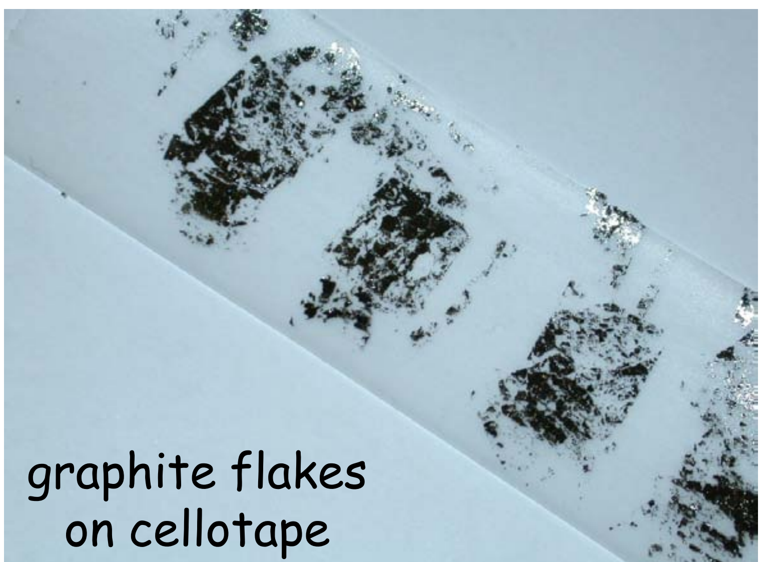
Esquinazi & Kopelevich 2000-2002

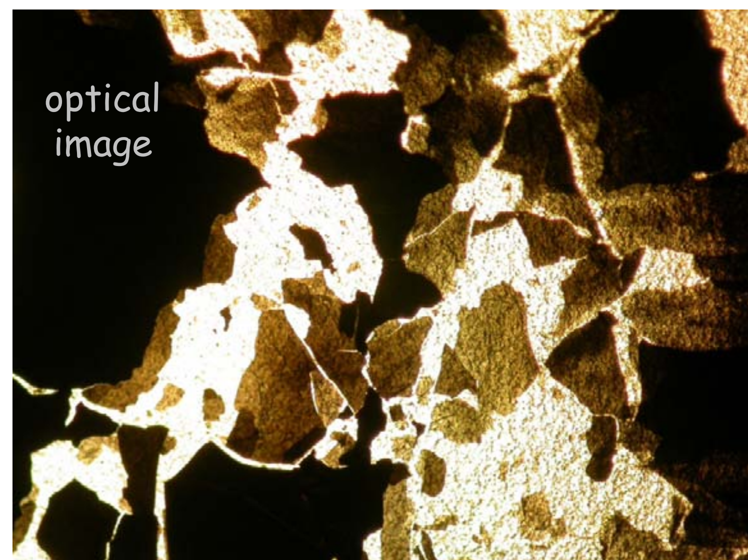
THE LEGEND OF SCOTCH TAPE

2002 PhD project of Da Jiang:
make graphite films
as thin as possible
and study
their "mesoscopic" properties
including electric field effect
& metallic transistor

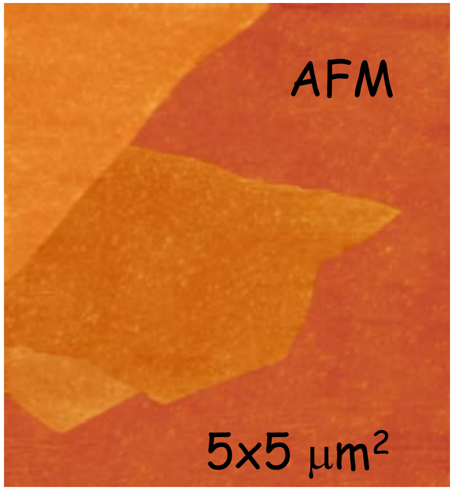


Oleg Shklyarevskii's idea



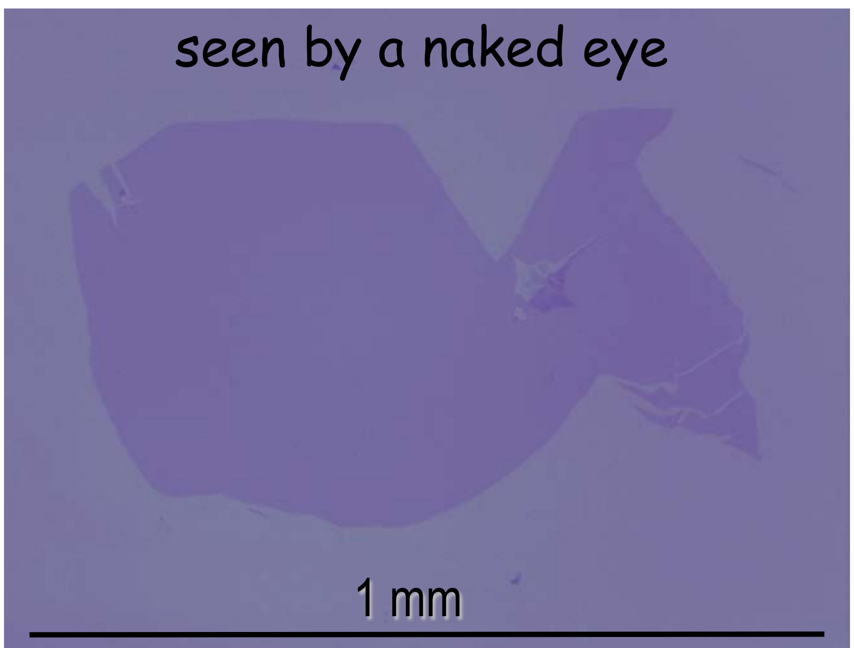


UNTIL A SINGLE LAYER FOUND



a few months later

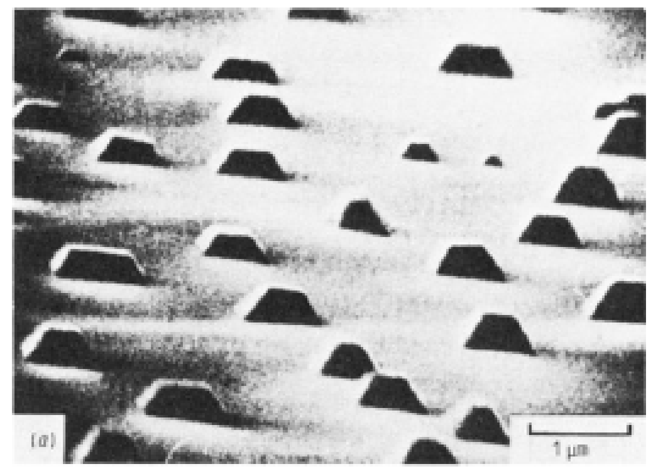
a few years later



SHOCK for INTUITION

background as of 2004:
thin film deposition &
semiconductor physics incl MBE

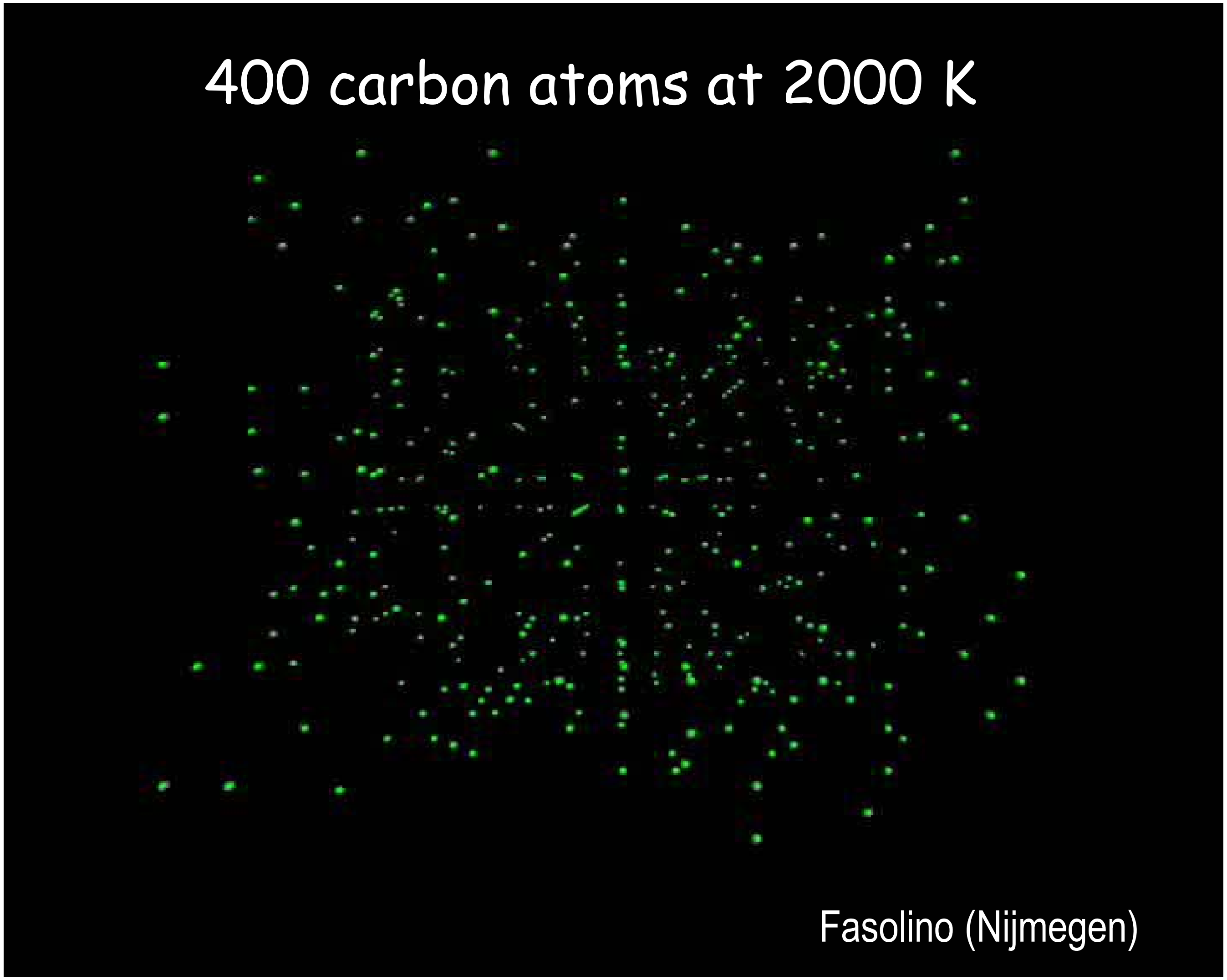
next to impossible to grow monolayers



Venables, Spiller, Hanbucken
Rep Prog Phys 1984

Komnik *Physics of Metal Films* 1979

2D GROWTH IS FORBIDDEN

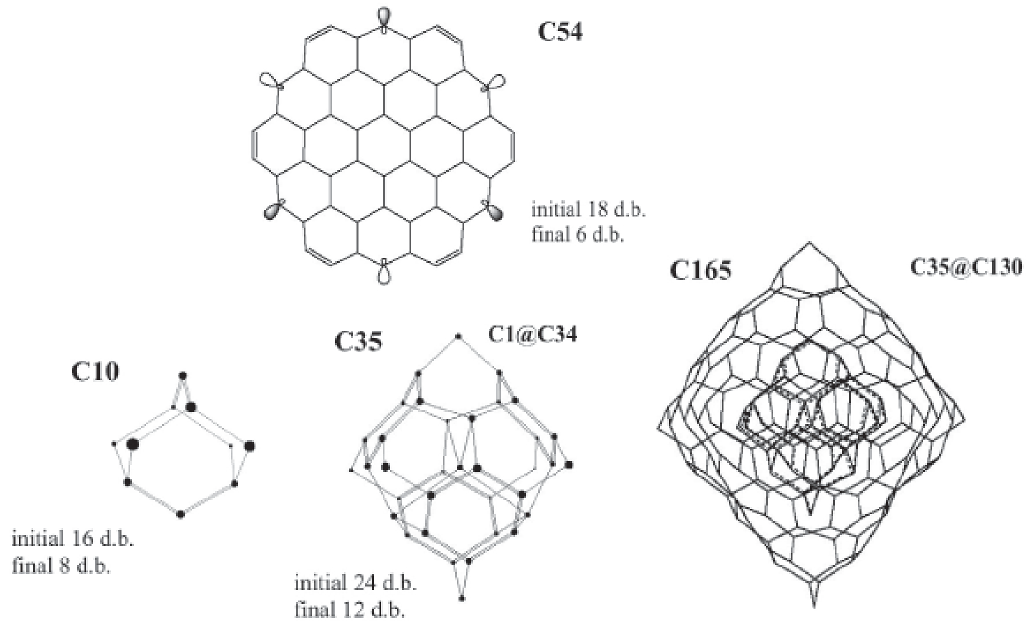


growth means *temperature close to melting* causes *violent vibrations* destroys *order in 2D*

Peierls; Landau; Mermin-Wagner; …

(only nm-scale flat crystals are possible to grow *in isolation*)

THERMODYNAMIC STABILITY

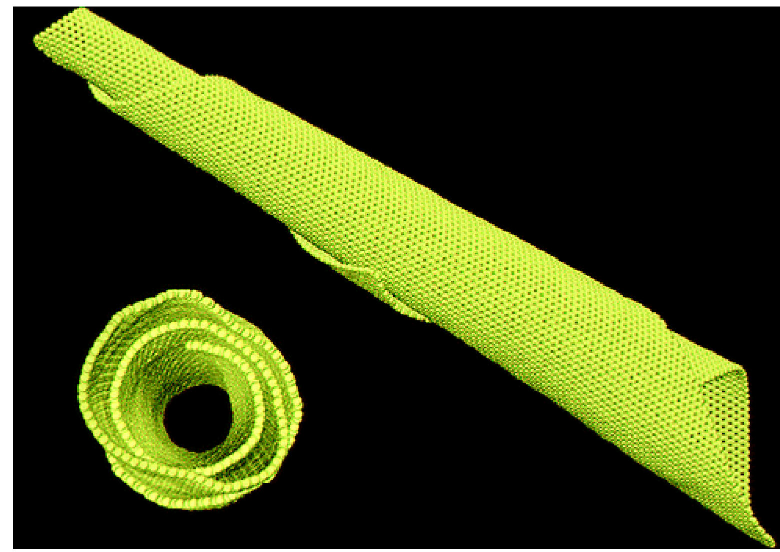


graphene:
thermodynamically unstable
for <24,000 atoms or size < 20 nm

Shenderova, Zhirnov, Brenner *Crit Rev Mat Sci* 2002

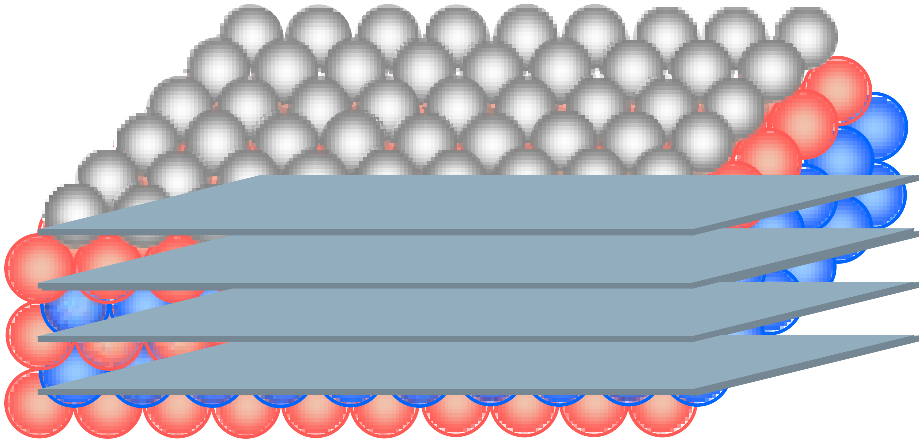
graphene sheets
should scroll

Kaner *Science* 2003
Braga *et al Nanolett* 2004



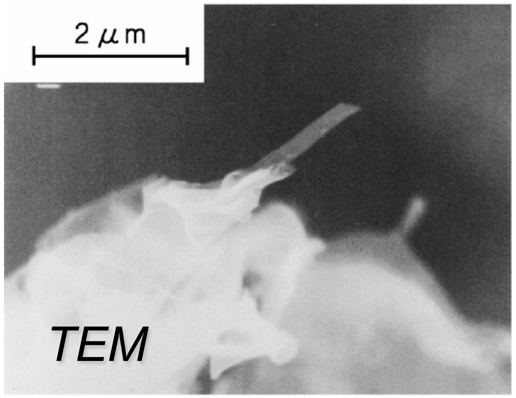
THERMODYNAMICALLY UNSTABLE
does not mean IMPOSSIBLE
-JUST METASTABLE-

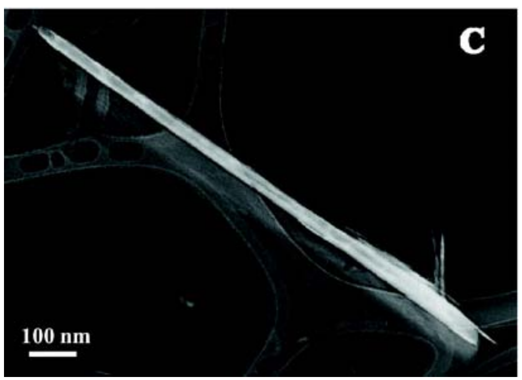
GRAPHENE VIA 3D GROWTH



HISTORY OF GRAPHENE

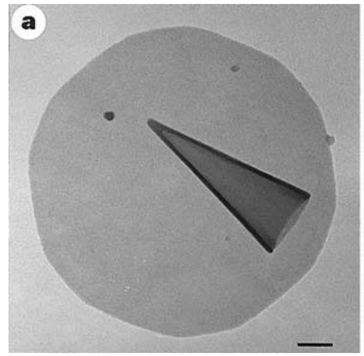
nanosrolls

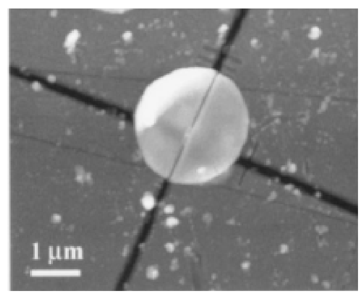




Shioyama *JMSL* 2001
Kaner *Science* 2003

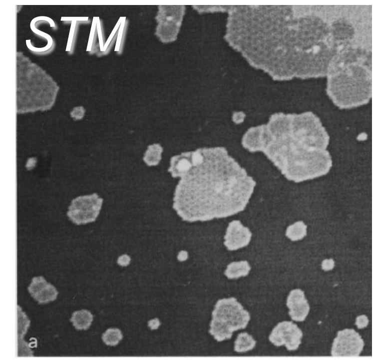
free growth



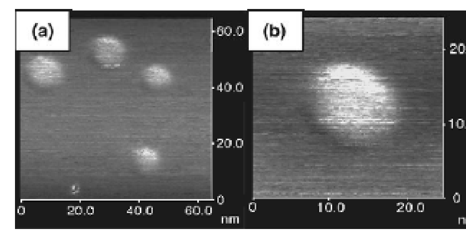


Ebbessen (~60 layers)
Nature 1997, *APL* 2001

substrate growth



graphene on metal:
Land *et al Surf Sci* 1992



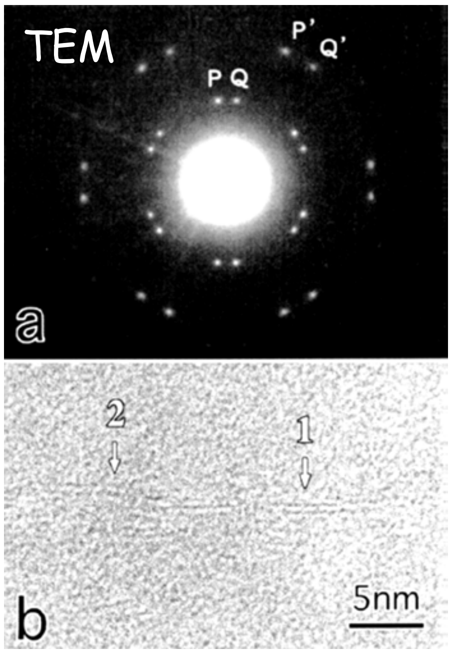
graphene on graphite:
Enoki *Chem. Phys. Lett. 2001*
J Phys 2002

as cited in our first paper in 2004

HISTORY OF GRAPHENE

intercalation

Frindt *Science* 1989
Horiuchi *et al* *APL* 2004

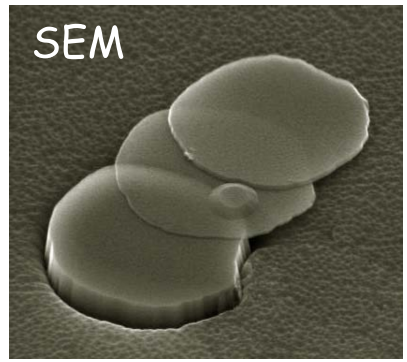


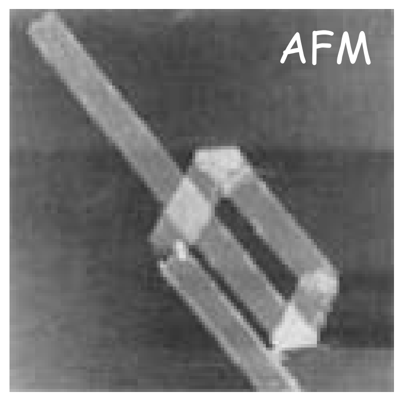
proof of isolated graphene

added along the same lines in our 2007 review

cleavage

Kurtz *PRB* 1990
Ebbesen *Adv Mat* 1995

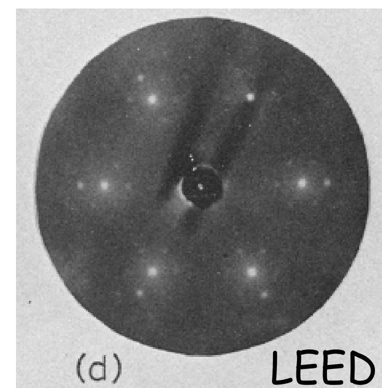




Ohashi *Tanso* 1997
Ruoff *APL* 1999
Gan *Surf Sci* 2003

substrate growth

Grant *Surf Sci* 1970 (on Ru/Rh)
Bommel *Surf Sci* 1975 (SiC)



McConville *PRB* 1986
Nagashima *Surf Sci* 1993
Forbeaux *PRB* 1998

DISCOVERY OF GRAPHENE

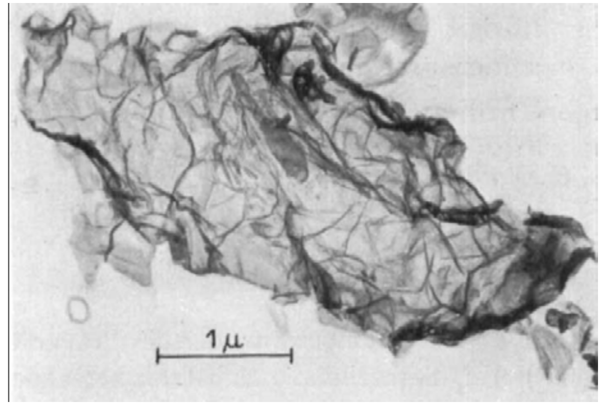
digging through old literature

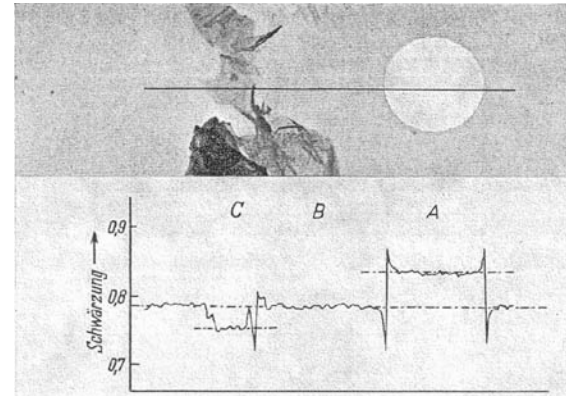
Benjamin Brodie
Phil Trans. 1859

"carbonic acid"

"Graphon 33"

suspension of graphene oxide crystallites



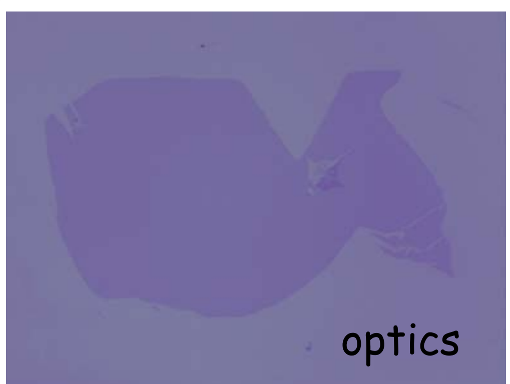


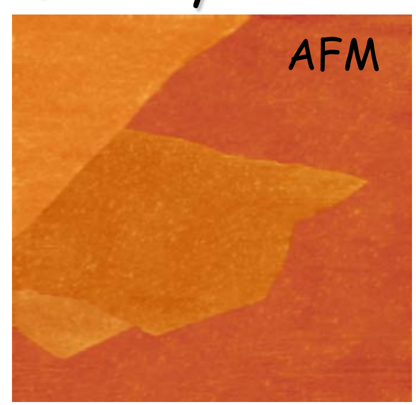
TEM studies of the dry residue

Ruess & Vogt 1948; Boehm & Hofmann 1962

remained the best observation for over 40 years!

2004: simple method of isolation of large crystals
unambiguous observations of monolayers

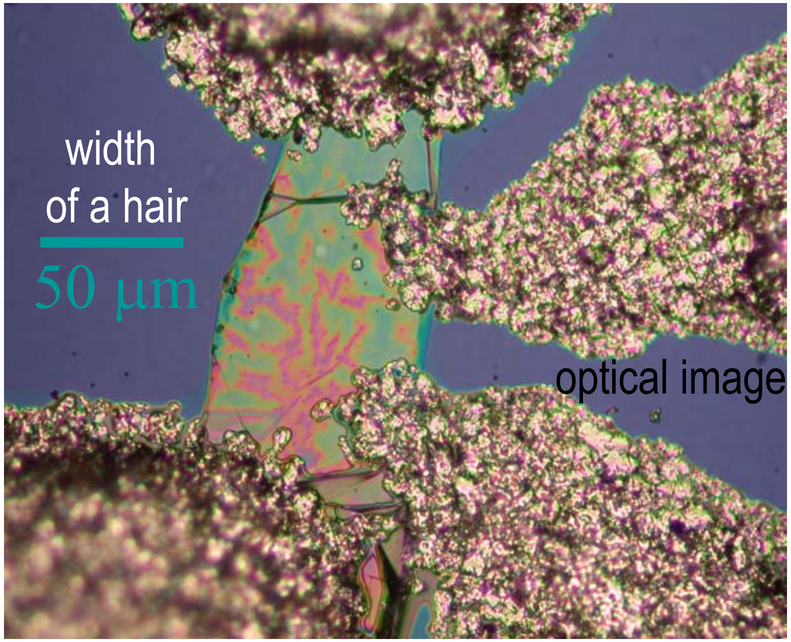




just observations: not enough to inspire further work

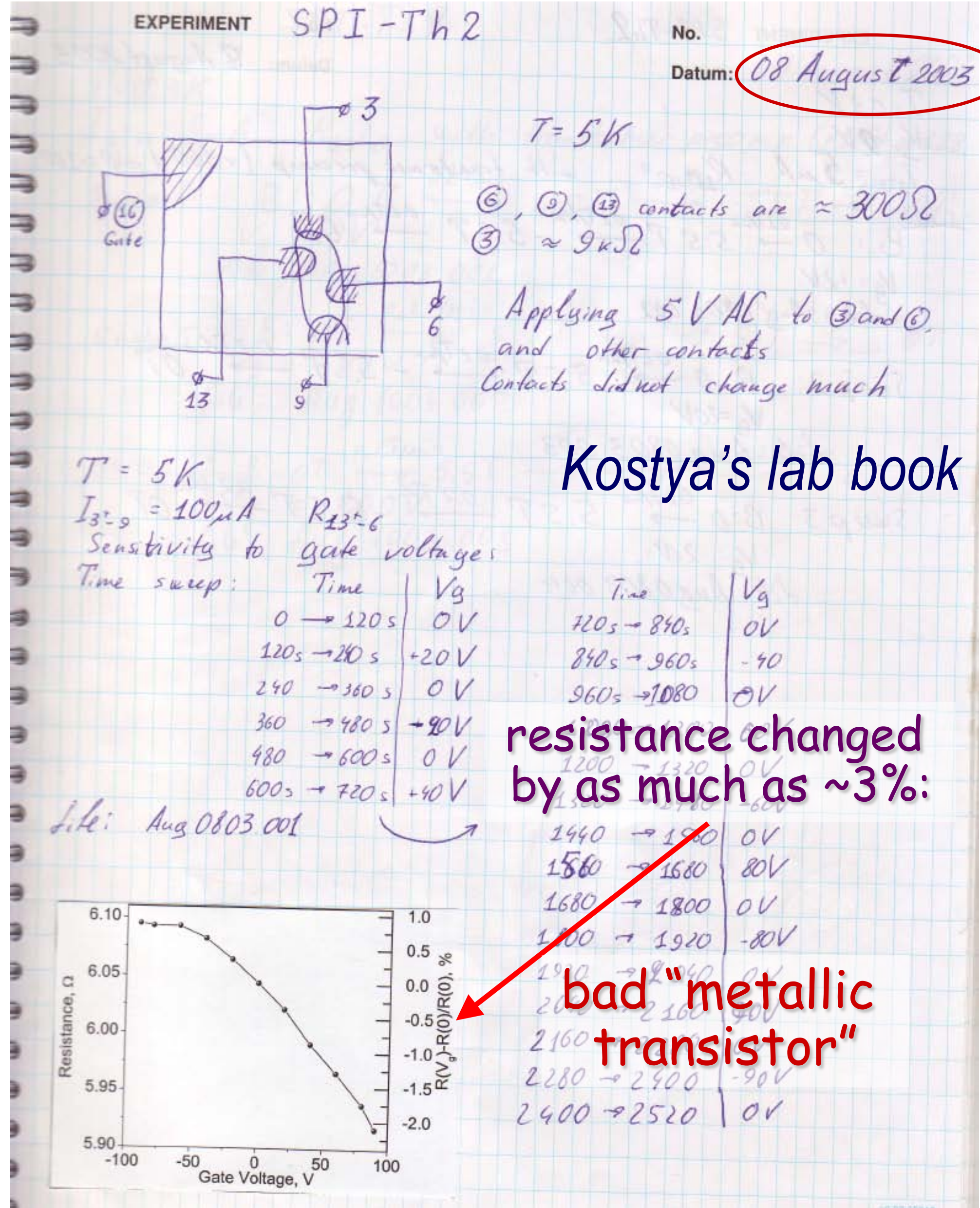
-OBLIVION-

BEYOND OBSERVATION



hand-made devices (Novoselov)
first on glass slides,
then on oxidized Si wafer

EUREKA MOMENT



Kostya's lab book

resistance changed by as much as ~3%:

bad "metallic transistor"

And after a lot of hard work …

down to a single layer; devices down to ~3 layers
on-off ratios ~30 at room *T* and >100 at low *T*

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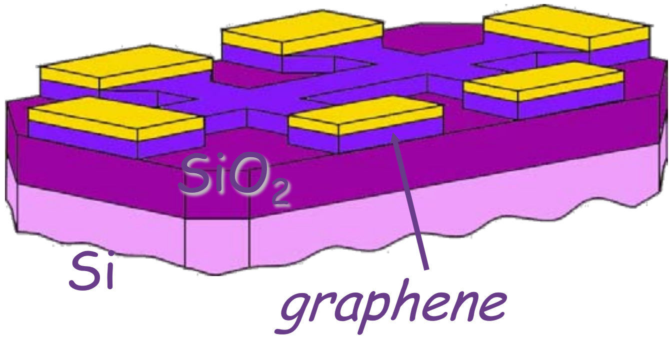
Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

N.B. twice rejected by *Nature*

WHY THIS PAPER IMPORTANT

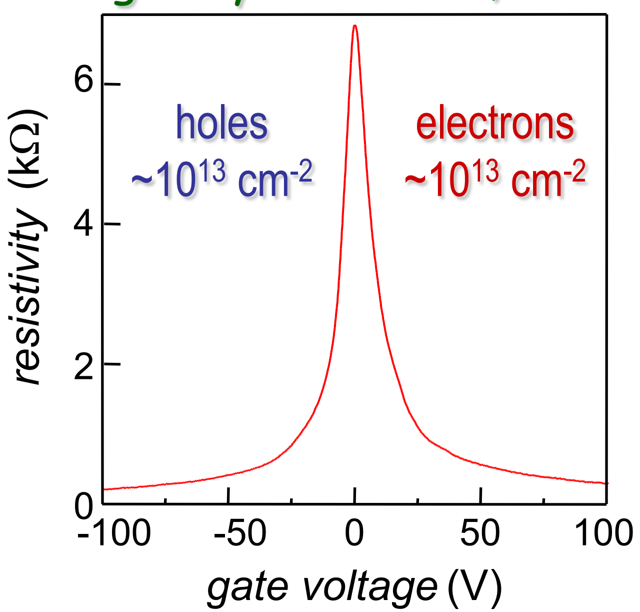
- observation of large isolated graphene crystals
- simple and accessible method for their isolation



- *CONTROL ELECTRONIC PROPERTIES*

ambipolar electric field effect

changes by 100 times, not ~1%



- *ASTONISHING ELECTRONIC QUALITY*

ballistic transport on submicron scale under ambient conditions

NOT JUST AN OBSERVATION OF GRAPHENE:

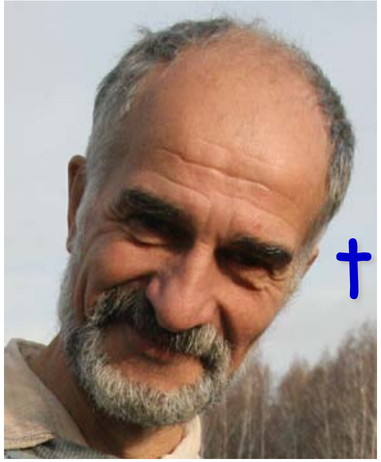
GRAPHENE REDISCOVERED IN ITS NEW INCARNATION

NEW HIGH QUALITY 2D ELECTRON SYSTEM & BEYOND

massless and massive Dirac fermions
two new types of the quantum Hall effect
metallic in the limit of no charge carriers
universal optical conductivity
defined by the fine structure constant
Klein tunnelling
tuneable-gap semiconductor
giant pseudo-magnetic fields by elastic strain
new type of chemistry: graphane & fluorographene
possibility of carving devices on a true nm scale
sensors capable of detecting individual gas molecules

… … … … …

many more beautiful observations by other groups



Sergey Dubonos
microfabrication

timeline finishes in mid 2004

Sergey Morozov
measurements

Irina Grigorieva
SEM, writing up

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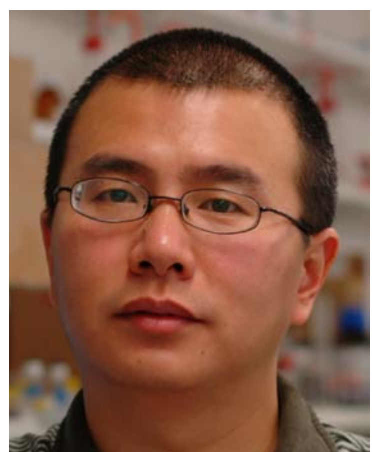
Yuan Zhang
microfabrication



Da Jiang
graphene crystallites

Anatoly Firsov
microfabrication