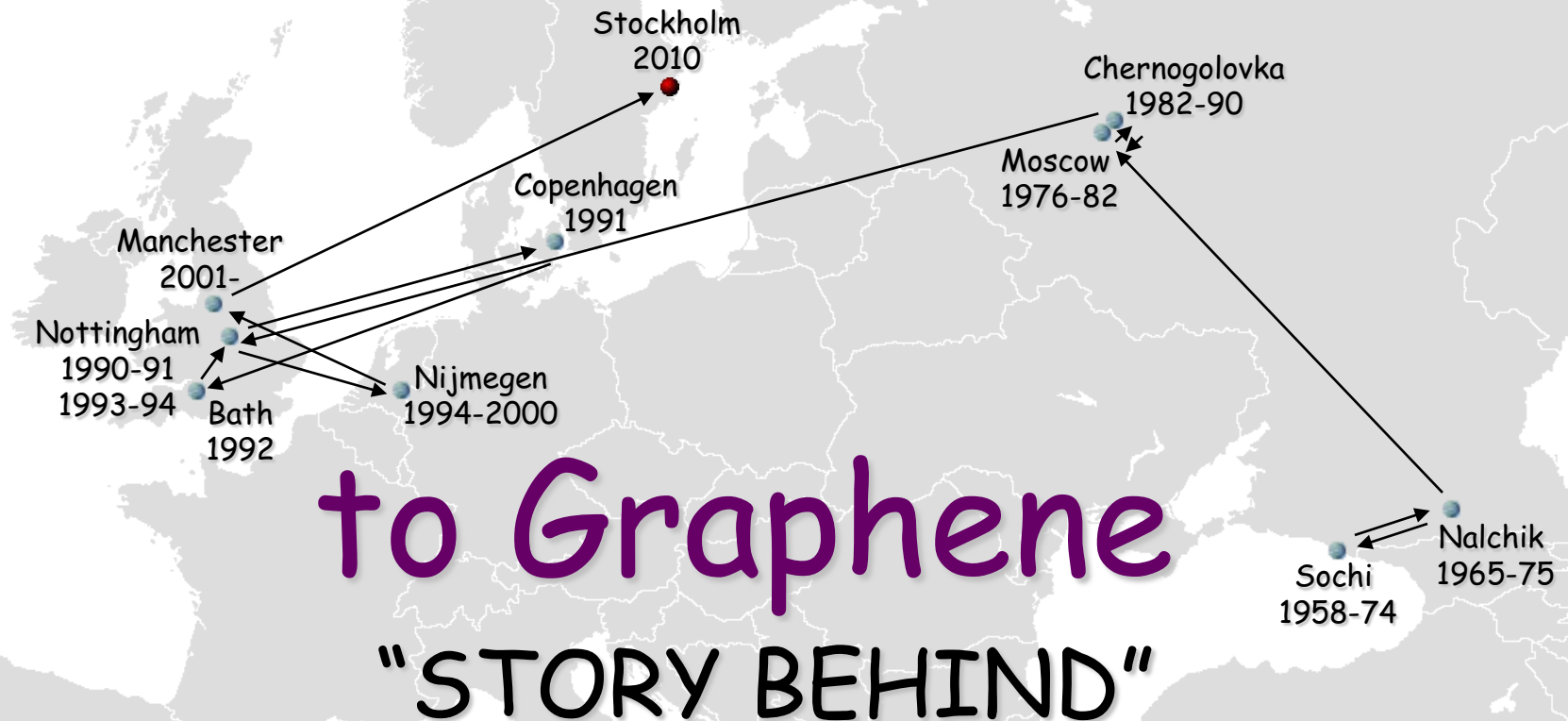


Random Walk



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”



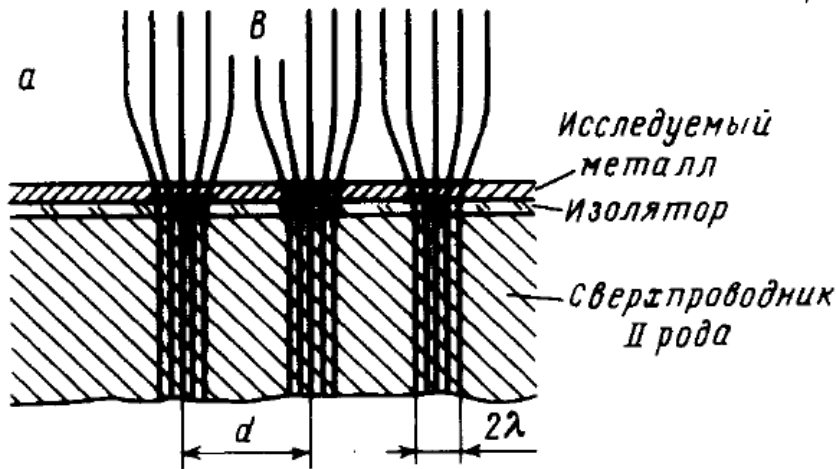
message I took away:
NEVER TORTURE
STUDENTS WITH
BORING/DEAD PROJECTS !

as exciting as it sounds

SWEET TASTE OF FREEDOM

staff scientist in Chernogolovka: 1988-1990

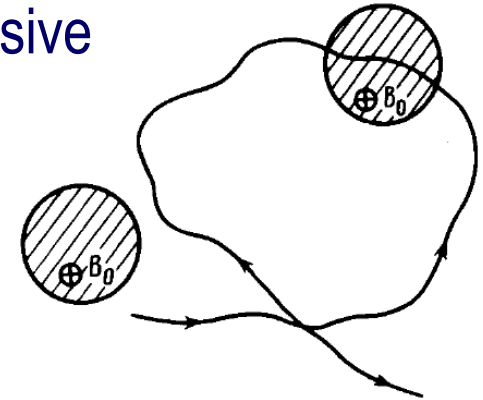
something new but still possible
with available Soviet facilities



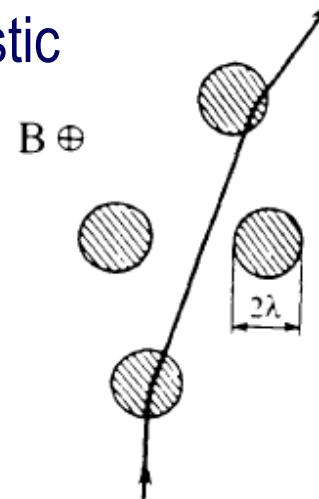
magnetic field inhomogeneous
on a submicron scale

experience I took away:
**NEW EXPERIMENTAL SYSTEM
IS BETTER THAN
A NEW PHENOMENON !**

diffusive



ballistic



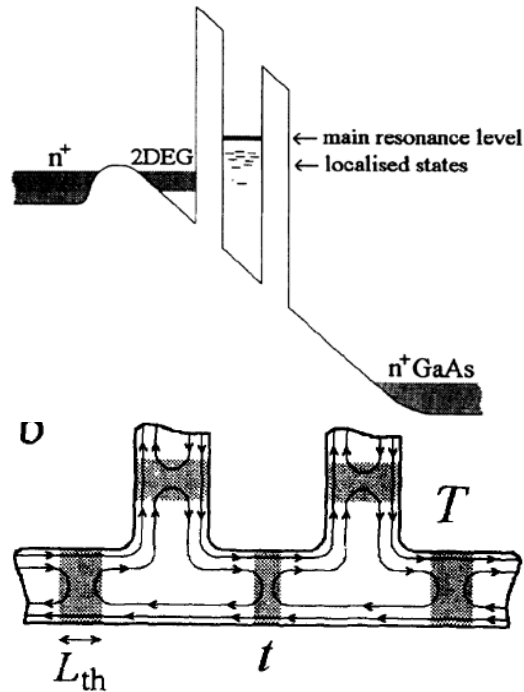
Geim, *JETP Lett.* 1989
Geim, **Sergey Dubonos** et al
JETP Lett. 1990
later, two *PRL* 1991, 1994

MOVING YEARS

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

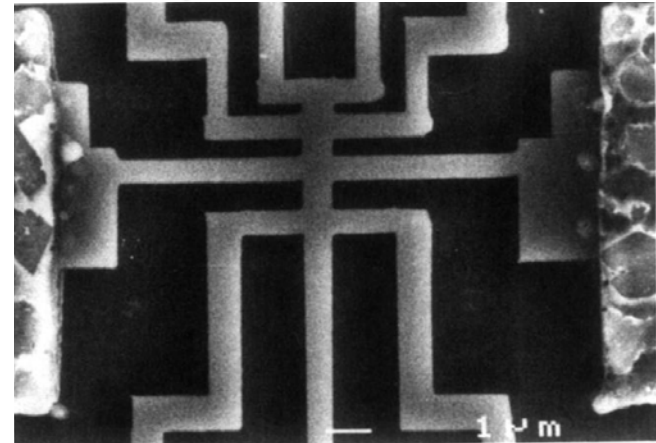
age = 32
h-index ~1

SEMICONDUCTOR PHYSICS



GaAs 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

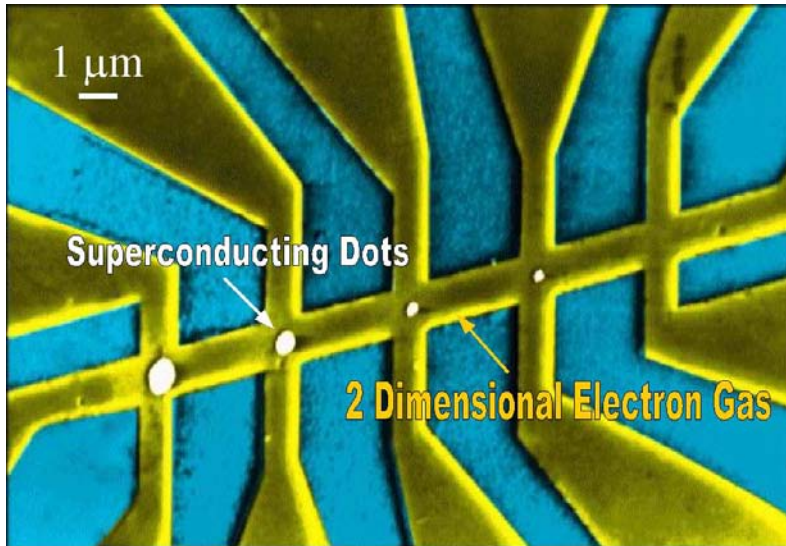
experience to tease colleagues:
"NO SUCH THING
AS BAD SAMPLES,
ONLY BAD POSTDOCS 😊"

GOING DUTCH

associate professor in Nijmegen: 1994-2000

FINDING RESEARCH NICHE:
possible but somewhat different

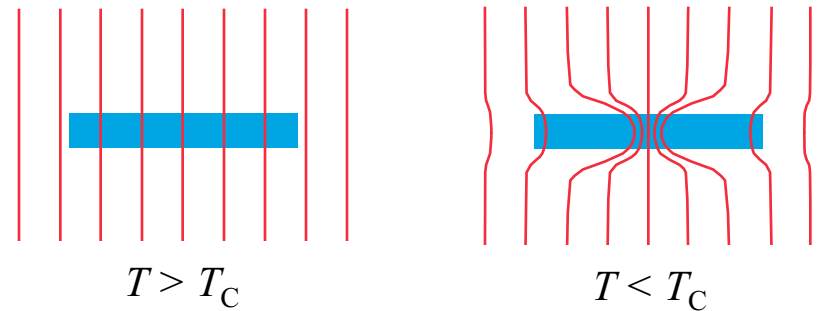
micron-sized Hall probes to investigate
superconductors, ferromagnetics, etc



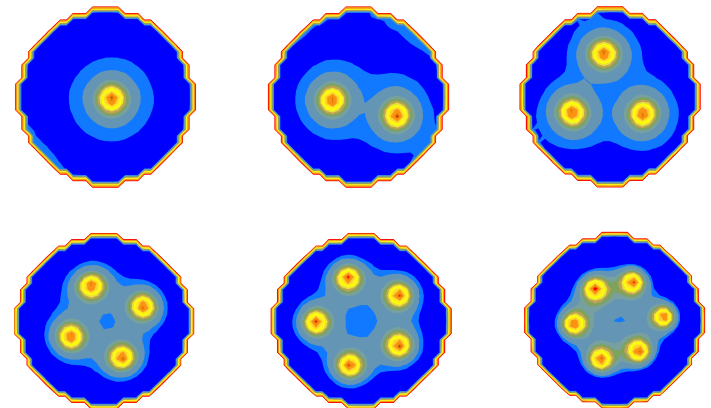
structures from Nottingham
lithography in Russia: **Sergey Dubonos**
measurements in Nijmegen

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"

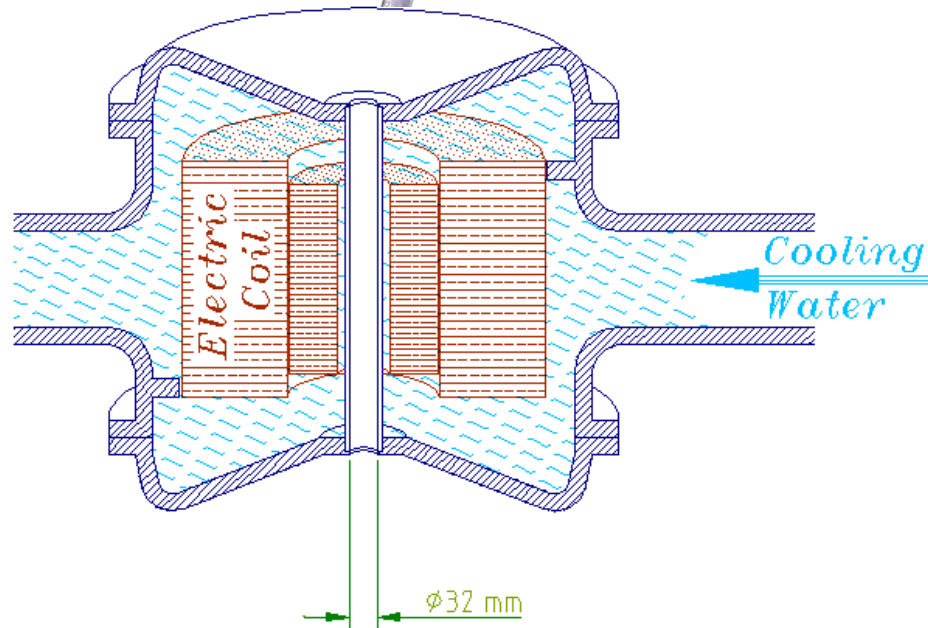
starting 1997



magnetic water descaler



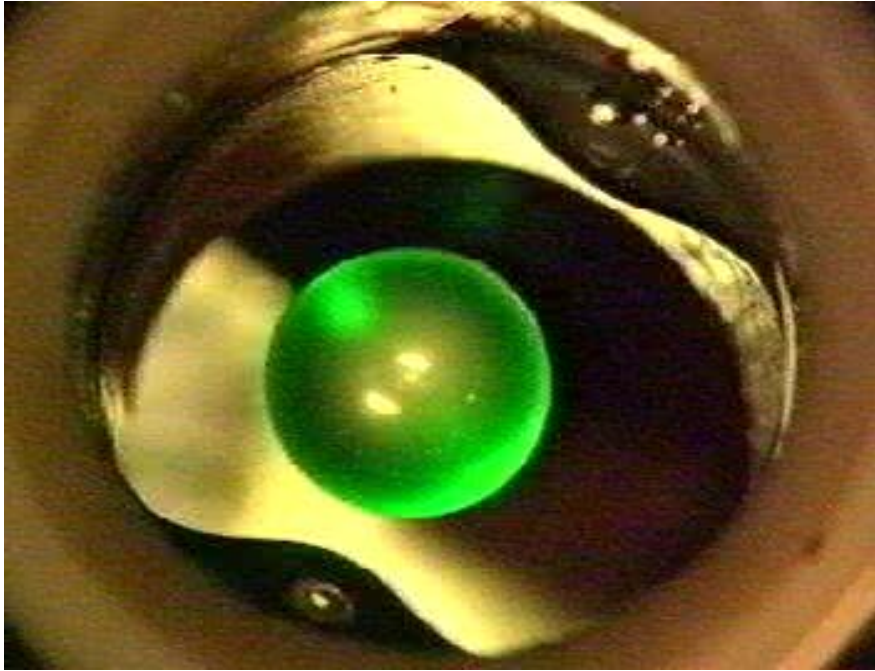
water in high magnetic fields?



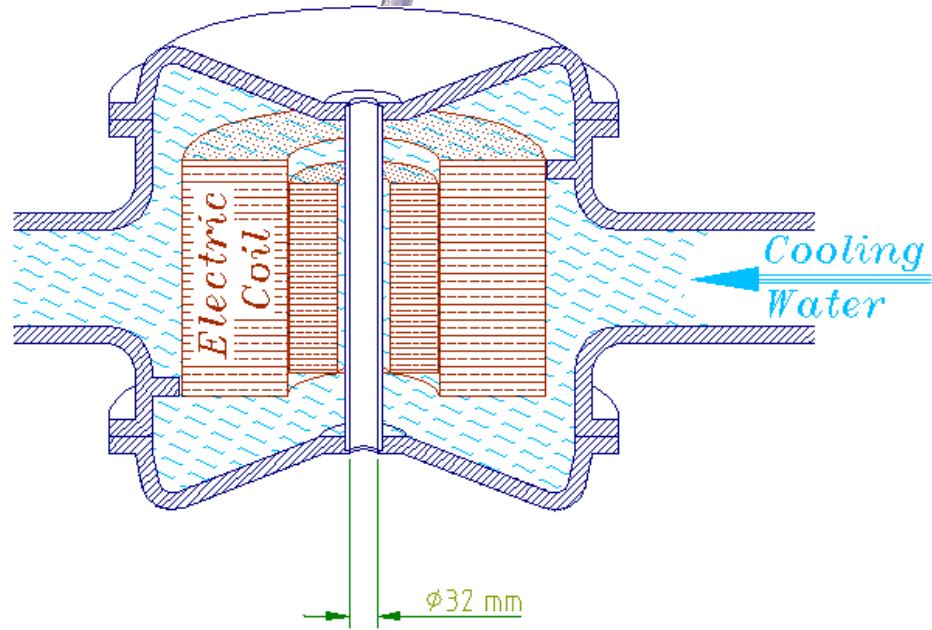
20T BITTER MAGNET

ancient magnets:
consume a lot of energy
require extra cryostats

A BIT OF LEVITY



water in high
magnetic
fields



20T BITTER MAGNET

NEEDS EMPHASIS

Levitation of organic materials

STR—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 $G_{\text{Bi}} = 729 \text{ T}^2 \text{ m}^{-1}$, $B_{\text{Bi}} = 15.87 \text{ T}$ and $G_{\text{Sb}} = 1,208 \text{ T}^2 \text{ m}^{-1}$, $B_{\text{Sb}} = 18.75 \text{ T}$, 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 $1,648 \text{ T}^2 \text{ m}^{-1} < G_s < 1,753 \text{ T}^2 \text{ m}^{-1}$, $21 \text{ T} <$

$B_s < 21.5 \text{ T}$ and $G_p = 1,923 \text{ T}^2 \text{ m}^{-1}$, $B_p = 22.28 \text{ T}$, respectively. Water, ethanol and acetone were levitated with $2,961 \text{ T}^2 \text{ m}^{-1} < G_s < 3,097 \text{ T}^2 \text{ m}^{-1}$, $26.5 < B_s < 27 \text{ T}$, $1,445 \text{ T}^2 \text{ m}^{-1} < G_c < 1,648 \text{ T}^2 \text{ m}^{-1}$, $20 \text{ T} < B_c < 21 \text{ T}$ and $1,862 \text{ T}^2 \text{ m}^{-1} < G_a < 2,086 \text{ T}^2 \text{ m}^{-1}$, $22 \text{ T} < B_a < 23 \text{ T}$, respectively. Values for the liquids were higher than expected and may result from wetting effects in the apparatus.

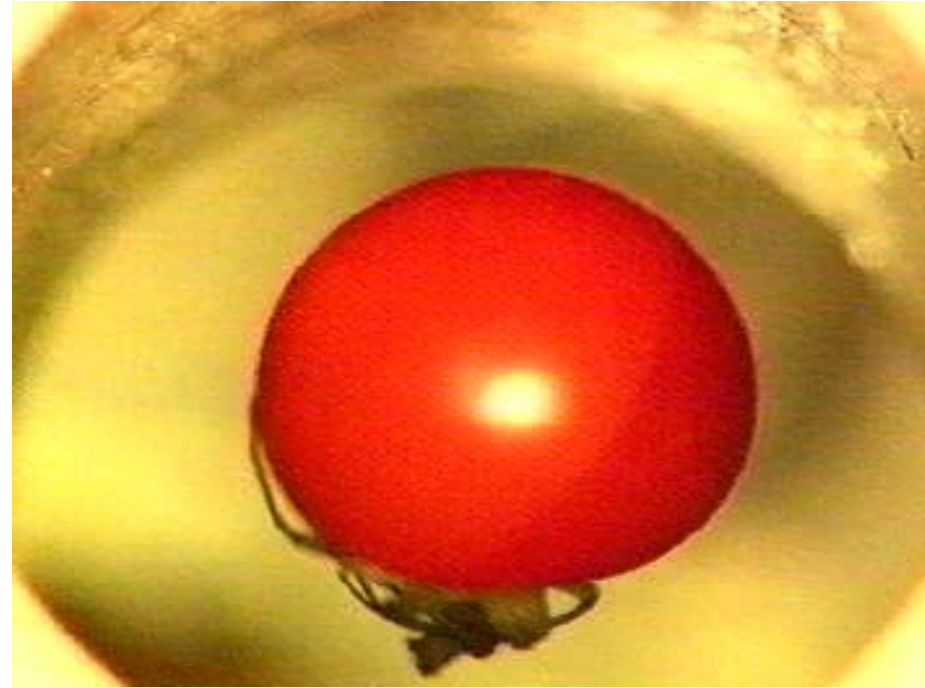
We have studied the levitation of graphite in a lower field magnet with a much larger bore ($G_g = 140 \text{ T}^2 \text{ m}^{-1}$ and $B_g = 5.25 \text{ T}$). We have confirmed that the levitation was very stable, without any contact with the magnet bore.

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 Recherche sur les
Très Basses Températures,
Laboratoire associé à l'université
Joseph Fourier,
25 Ave des Martyrs,
38042 Grenoble Cedex, France

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

Scientists magnetised by levitating frog

The Independent 12/04/97

Charles Arthur
Science Editor

NEWS OF THE WORLD, October 5, 1997

INCREDIBLE!

Animal magnetism machine 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.



LEVITY

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

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, much like Jean-Claude Van Damme. What did the scientists expect the frog to do? Hop around

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 in by a number of alert readers, Dutch scientists "have succeeded in levitating a frog in air." They used a technique called "animal magnetism," which, as you know, is the same as the "animal magnetism" that is used for magnetic levitation. How many times 7 goes into 56; naturally. 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 FOR SCHOOL!" you could waste your time yelling, "STOP DRAWING ON THAT MARKING PEN ON THE WALL!" So perhaps this is a good use for magnetic levitation.

APRIL 12, 1997
It's all up in the air
Frog floats through

The Guardian
April 12, 1997

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

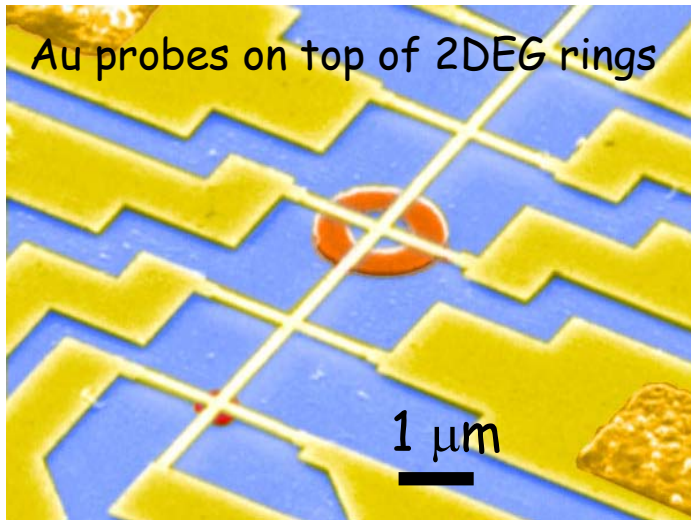
MANCUNIAN WAY

chair in Manchester: 2001 - present

empty lab; little start-up; no central microfabrication

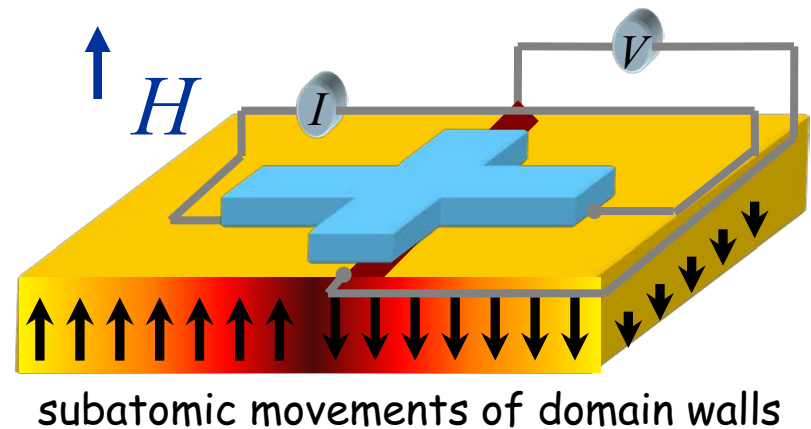
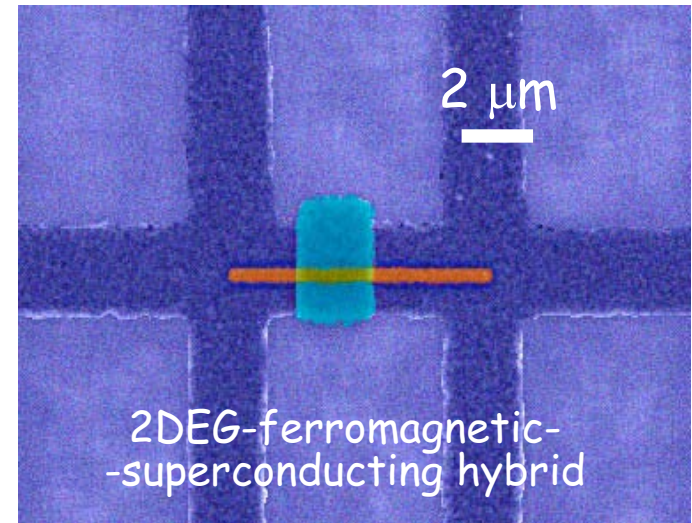
FIRST ESTABLISH YOURSELF & SET UP NEW FACILITIES

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



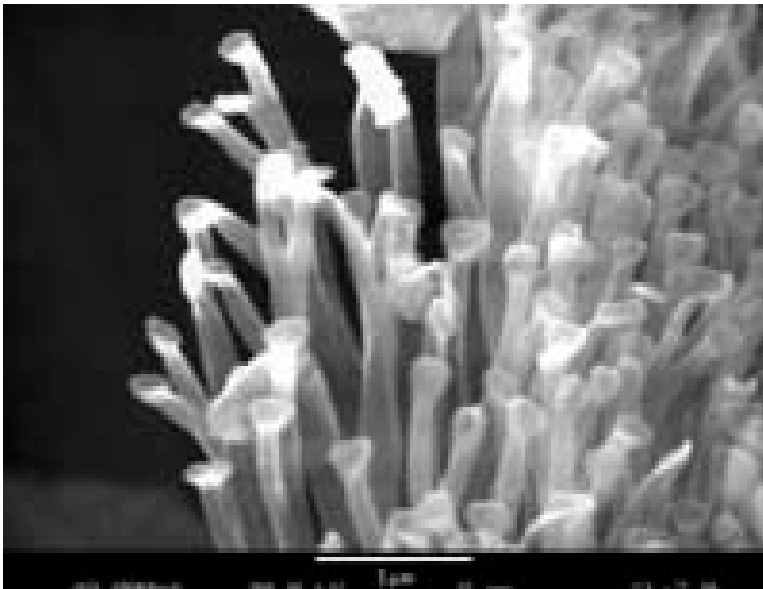
"FRIDAY NIGHTS" in MANCHESTER

HOW COMES THAT GECKO CAN CLIMB WALLS?



"FRIDAY NIGHTS" in MANCHESTER

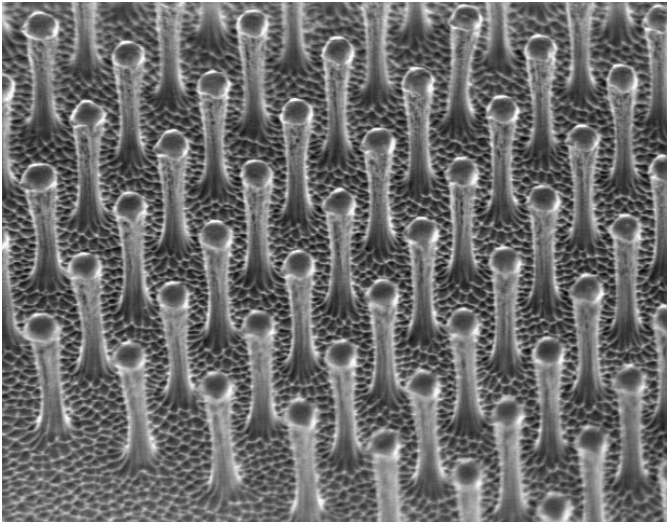
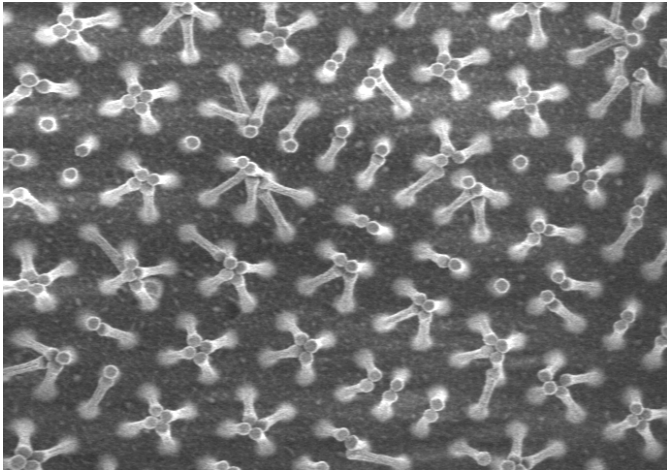
*sticky feet:
geckos climb due to their hairy toes*



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

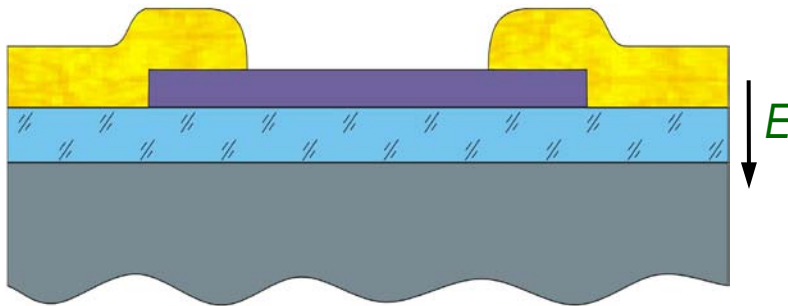
One Little Thought Cloud

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 $\sim 1\text{V/nm}$
max induced concentration $\approx 10^{14}\text{ cm}^{-2}$

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

One Little Thought Cloud

metallic electronics

Schlesinger 2000
Lemanov & Kholkin 1994
Petrashov 1991

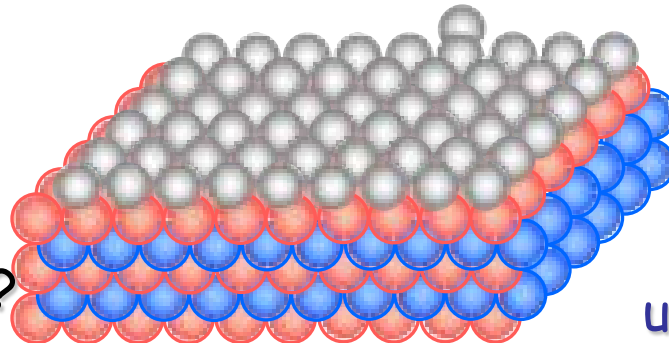
...
Bose (1906)
Mott (1902)

**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

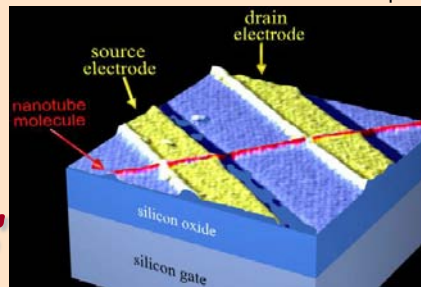
Two More Little Clouds

metallic electronics

Schlesinger 2000
Lemanov & Kholkin 1994
Petrashov 1991

...
Bose (1906)
Mott (1902)

carbon nanotube transistors



Ijima, Ebbesen, McEuen
Dekker, Avouris

Dresselhaus' review 1981

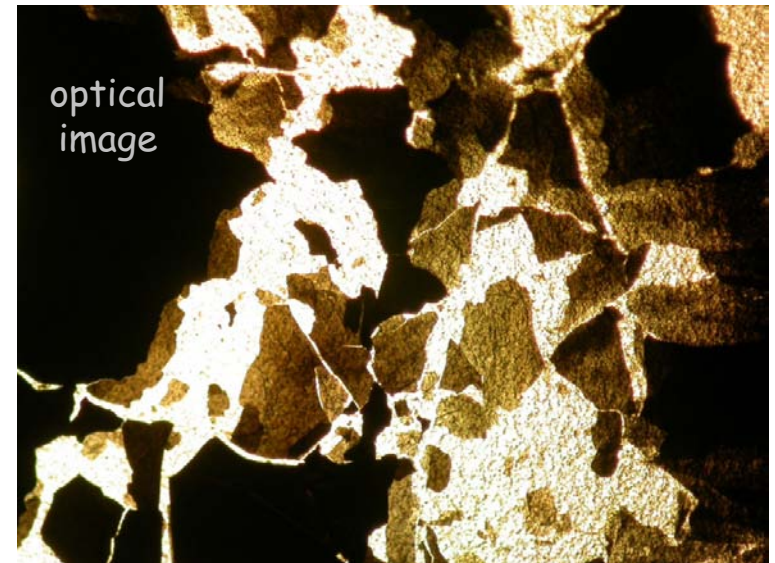
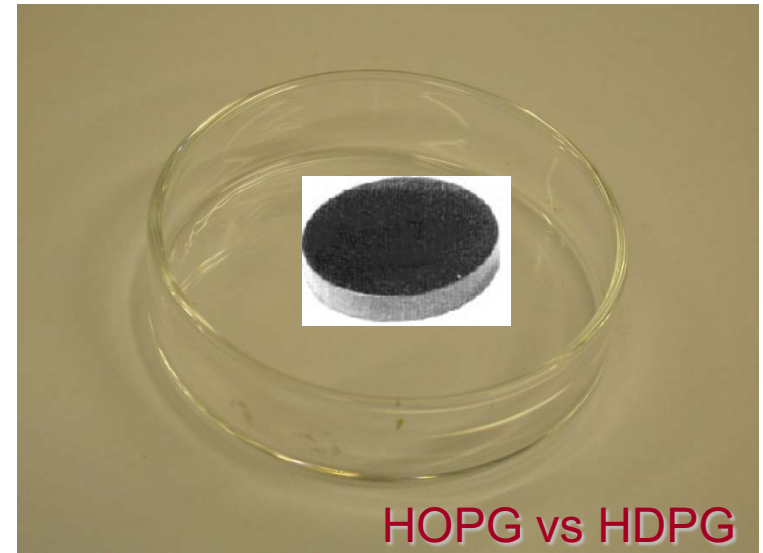
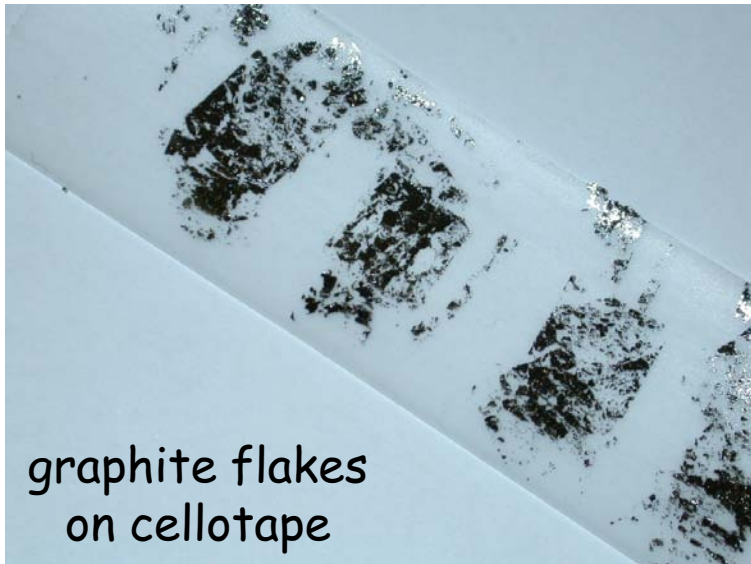
little known about thin films of graphite

Esquinazi & Kopelevich 2000-2002

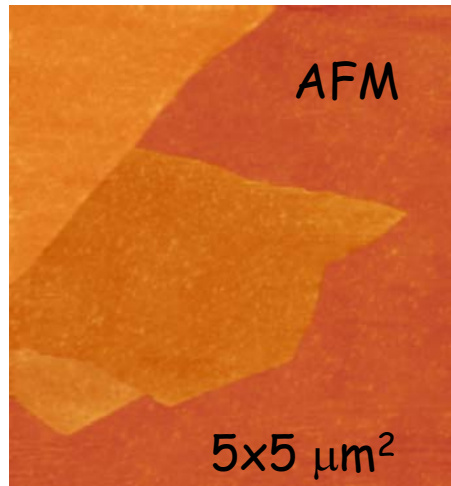
THE LEGEND OF SCOTCH TAPE

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

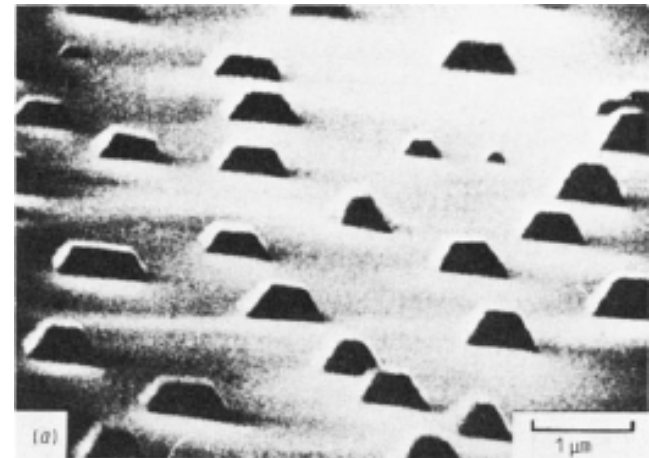
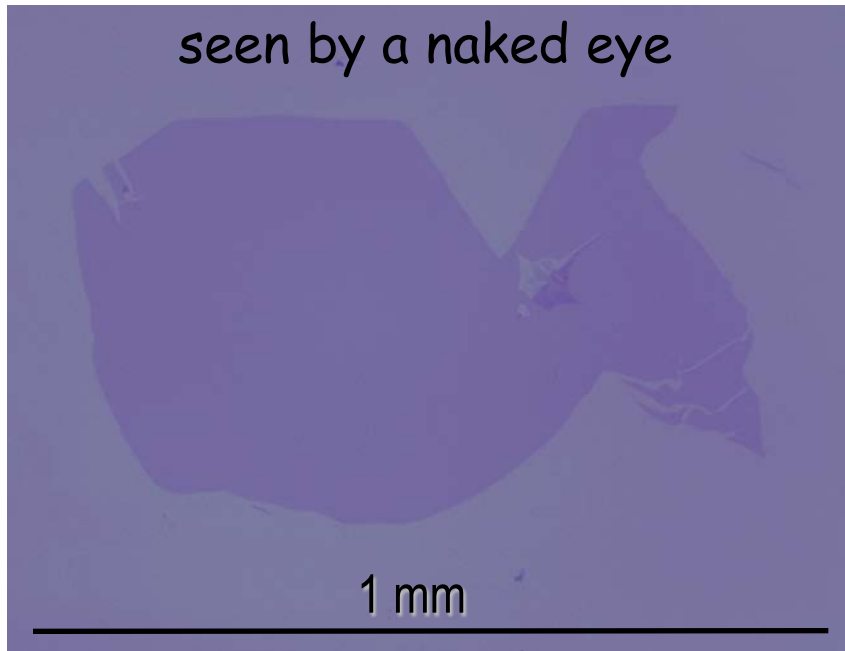
SHOCK for INTUITION

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

next to impossible
to grow monolayers

a few years later

seen by a naked eye

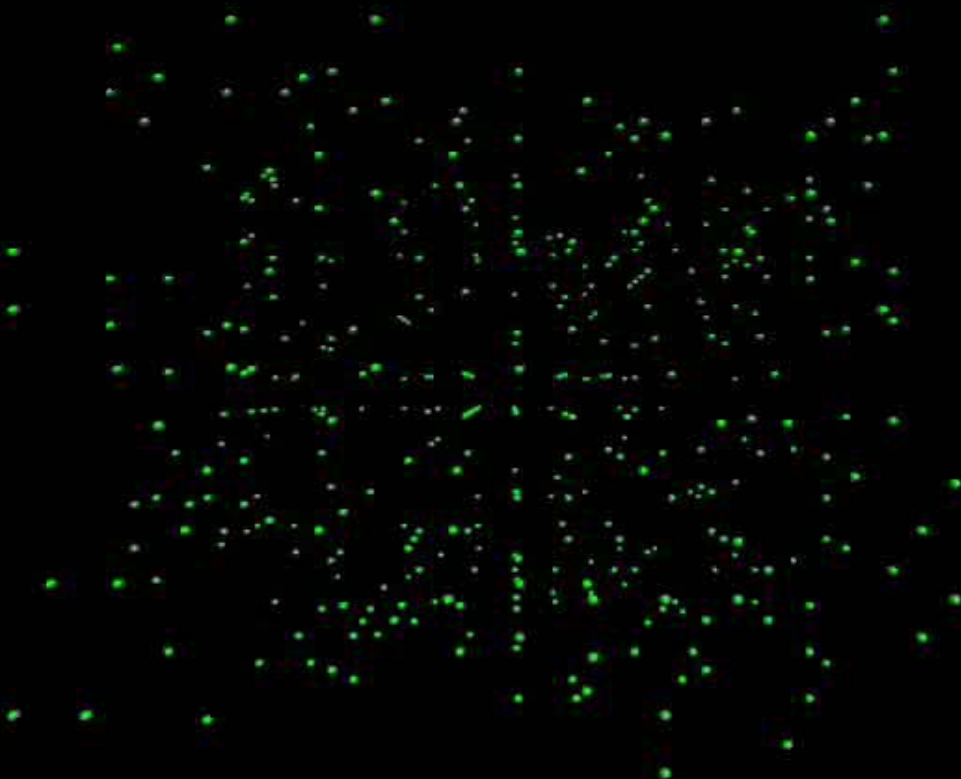


Venables, Spiller, Hanbucken
Rep Prog Phys 1984

Komnik *Physics of Metal Films* 1979

2D GROWTH IS FORBIDDEN

400 carbon atoms at 2000 K

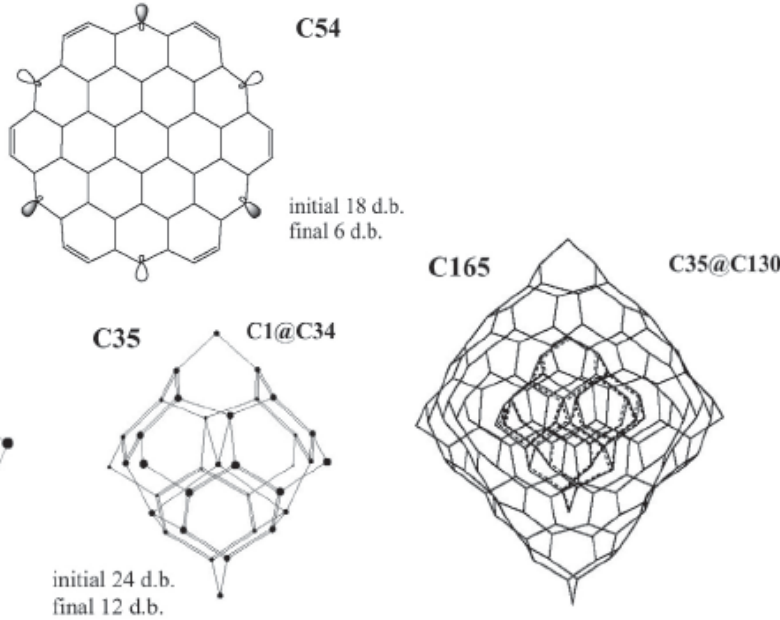


Fasolino (Nijmegen)

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 sheets
should scroll
Kaner *Science* 2003
Braga *et al Nanolett* 2004

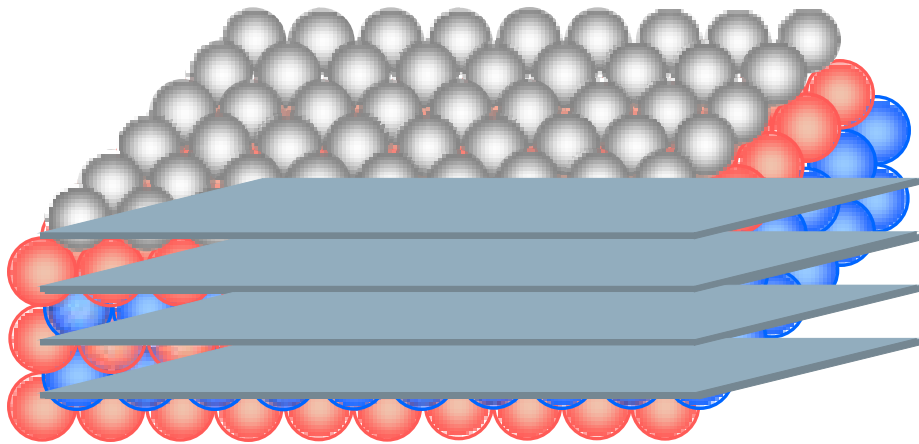


graphene:
thermodynamically unstable
for <24,000 atoms or size < 20 nm

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

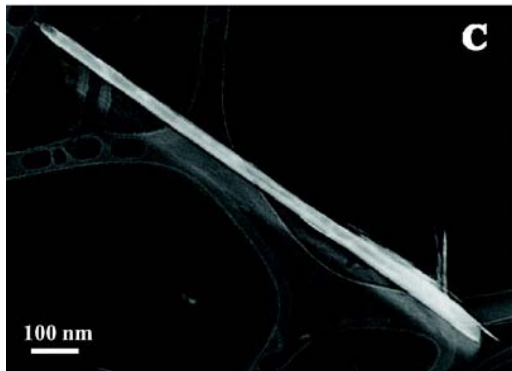
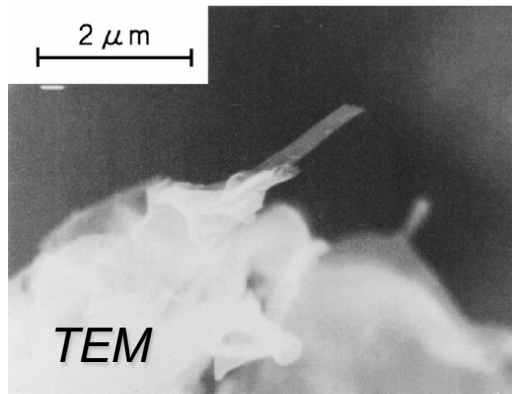
THERMODYNAMICALLY UNSTABLE
does not mean IMPOSSIBLE
-JUST METASTABLE-

GRAPHENE VIA 3D GROWTH



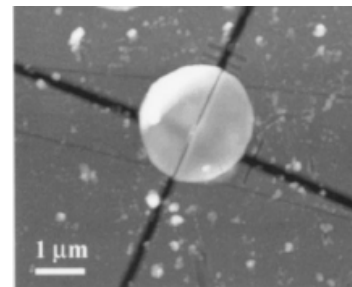
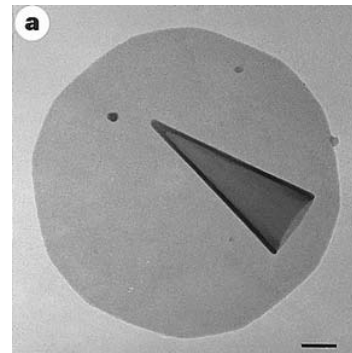
HISTORY OF GRAPHENE

nanoscrolls



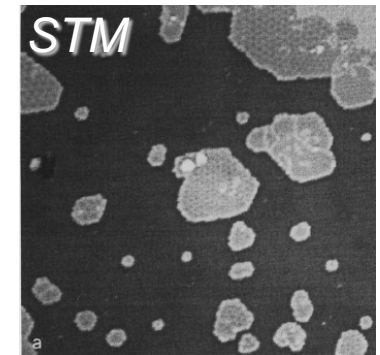
Shioyama *JMSL* 2001
Kaner *Science* 2003

free growth

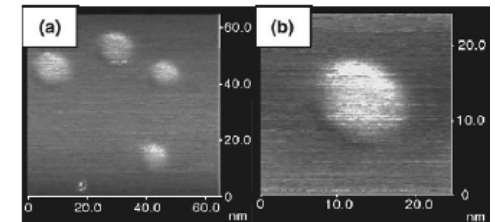


Ebbesen (~60 layers)
Nature 1997, *APL* 2001

substrate growth



graphene on metal:
Land et al Surf Sci 1992



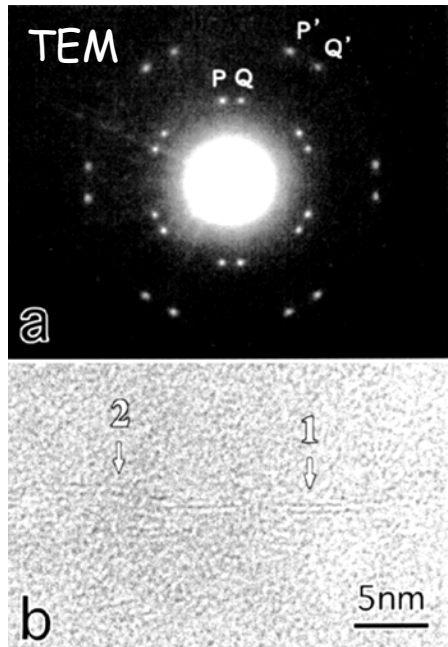
graphene on graphite:
Enoki Chem. Phys. Lett. 2001
J Phys 2002

as cited in our first paper in 2004

HISTORY OF GRAPHENE

intercalation

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

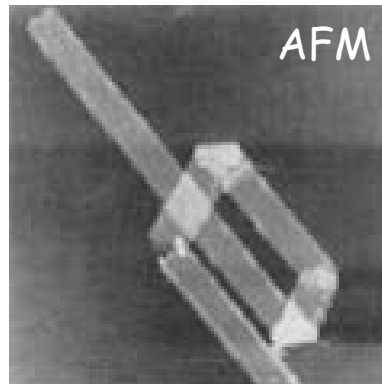
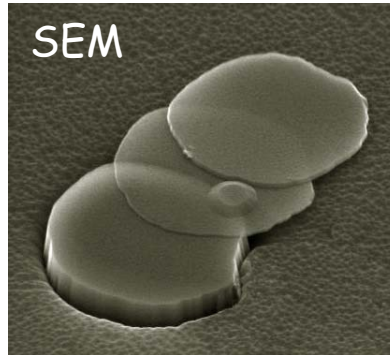


proof of isolated graphene

added along
the same lines in
our 2007 review

cleavage

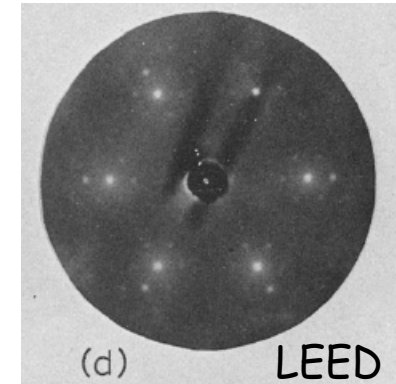
Kurtz *PRB* 1990
Ebbesen *Adv Mat* 1995



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

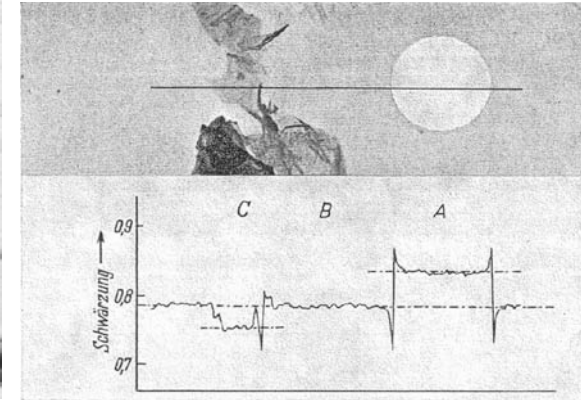
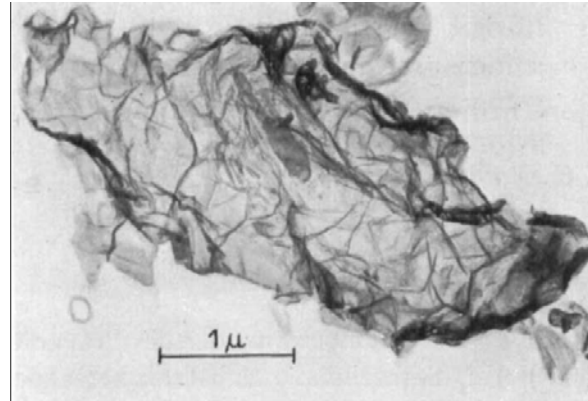


Benjamin Brodie
Phil Trans. 1859

"carbonic acid"

"Graphon 33"

suspension of
graphene oxide
crystallites

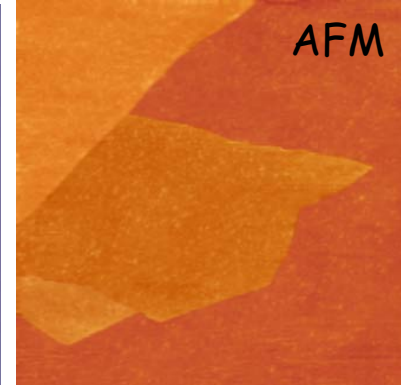
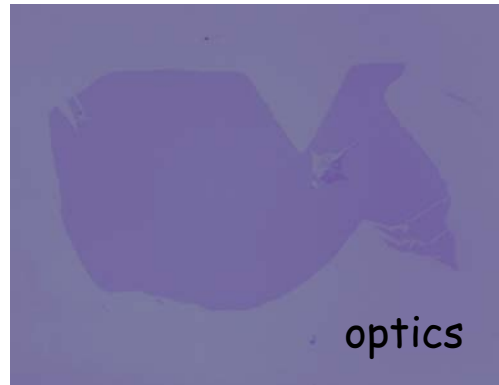


TEM studies of the dry residue

Ruess & Vogt 1948; Boehm & Hofmann 1962

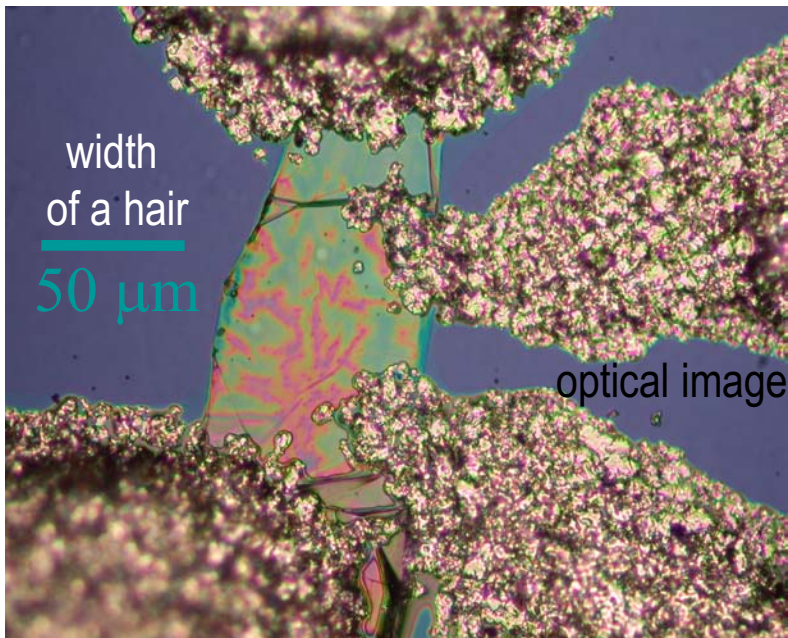
remained the best observation for over 40 years!

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



just
observations:
not enough
to inspire
further work
-OBLIVION-

BEYOND OBSERVATION



width of a hair
50 μm

optical image

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

EUREKA MOMENT

EXPERIMENT SPI-Th2

No. _____
Datum: 08 August 2003

$T = 5\text{K}$

⑥, ⑨, ⑬ contacts are $\approx 300\Omega$
③ $\approx 9\text{k}\Omega$

Applying 5V AC to ③ and ⑥
and other contacts
Contacts did not change much

$T = 5\text{K}$
 $I_{3-9} = 100\mu\text{A}$ R_{13-6}
Sensitivity to gate voltages
Time sweep:

Time	V_g	Time	V_g
0 \rightarrow 120 s	0V	1200 \rightarrow 1320	0V
120 s \rightarrow 240 s	+20V	1320 \rightarrow 1440	0V
240 \rightarrow 360 s	0V	1440 \rightarrow 1560	80V
360 \rightarrow 480 s	+80V	1560 \rightarrow 1680	0V
480 \rightarrow 600 s	0V	1680 \rightarrow 1800	0V
600 \rightarrow 720 s	+40V	1800 \rightarrow 1920	-80V
		1920 \rightarrow 2040	0V
		2040 \rightarrow 2160	80V
		2160 \rightarrow 2280	0V
		2280 \rightarrow 2400	-80V
		2400 \rightarrow 2520	0V

Life: Aug 0803 001

resistance changed by as much as $\sim 3\%$:

bad "metallic transistor"

Resistance, Ω

Gate Voltage, V

$\frac{R(V_g) - R(0)}{R(0)}, \%$

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

22 OCTOBER 2004 VOL 306 SCIENCE www.sciencemag.org

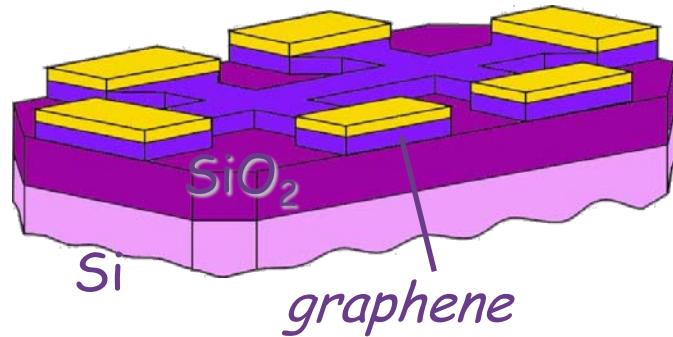
Electric Field Effect in Atomically Thin Carbon Films

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. Firsov²

N.B. twice rejected by Nature

WHY THIS PAPER IMPORTANT

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

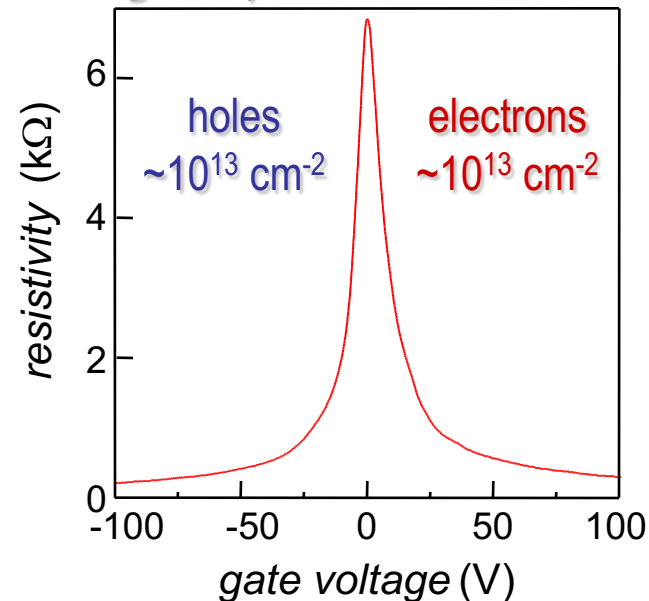


- **CONTROL ELECTRONIC PROPERTIES**
ambipolar electric field effect

- **ASTONISHING ELECTRONIC QUALITY**
ballistic transport on submicron scale
under ambient conditions

NOT JUST AN
OBSERVATION OF GRAPHENE:
GRAPHENE REDISCOVERED
IN ITS NEW INCARNATION

changes by 100 times, not ~1%



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

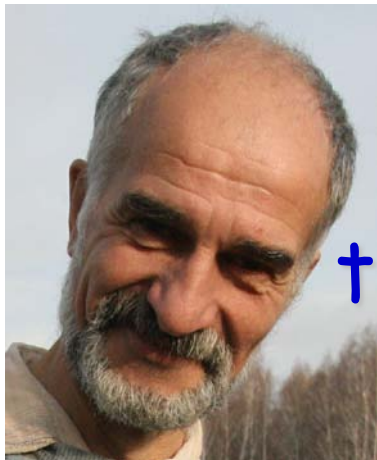
new type of chemistry: graphane & fluorographene

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



Sergey Morozov
measurements



Irina Grigorieva
SEM, writing up

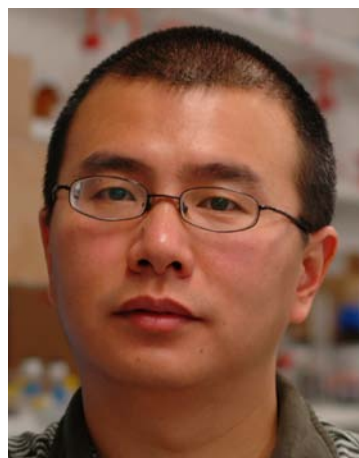
timeline finishes in mid 2004

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Yuan Zhang
microfabrication



Da Jiang
graphene
crystallites



Anatoly Firsov
microfabrication