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”

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

as exciting as it sounds
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!
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

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

submicron GaAs wires from a drawer

Geim, Laurence Eaves, Peter Main et al

my first 6-month visit
fractional flux vortices & vortex shells

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

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

writing up with Irina Grigorieva:

“FRIDAY NIGHT EXPERIMENTS”

starting 1997

water in high magnetic fields?

ancient magnets:
consume a lot of energy
require extra cryostats

magnetic water descaler

20T BITTER MAGNET

Cooling Water

φ32 mm
A BIT OF LEVITY

water in high magnetic fields

20T BITTER MAGNET
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 $G_{Bi} = 729 \, \text{T}^2 \, \text{m}^{-1}$, $B_{Bi} = 15.87 \, \text{T}$ and $G_{Sb} = 1,208 \, \text{T}^2 \, \text{m}^{-1}$, $B_{Sb} = 18.75 \, \text{T}$, respectively, values in very good agreement with calculations based on magnetic susceptibility data (R. C. Wcast, Handbook of Chemistry and Physics 1972–73). Pieces of wood and plastic were levitated with $1,648 \, \text{T}^2 \, \text{m}^{-1} < G < 1,753 \, \text{T}^2 \, \text{m}^{-1}$, $21 \, \text{T} < B < 21.5 \, \text{T}$ 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 $2,961 \, \text{T}^2 \, \text{m}^{-1} < G < 3,097 \, \text{T}^2 \, \text{m}^{-1}$, $26.5 \, \text{T} < B < 27 \, \text{T}$, $1,445 \, \text{T}^2 \, \text{m}^{-1} < G < 1,648 \, \text{T}^2 \, \text{m}^{-1}$, $20 \, \text{T} < B < 21 \, \text{T}$ and $1,862 \, \text{T}^2 \, \text{m}^{-1} < G < 2,086 \, \text{T}^2 \, \text{m}^{-1}$, $22 \, \text{T} < B < 23 \, \text{T}$, 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 ($G = 140 \, \text{T}^2 \, \text{m}^{-1}$ and $B = 5.25 \, \text{T}$). 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

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KNOWLEDGE IS FUN
WOW! FACTOR
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.

INCREDiBLE!

Animal magnetism machine.

Frog float in thin

Gravity is leap-frogged by a magnet.

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.

That’s right. They have levitated a frog.

According to an Associated Press report, Dutch scientists “have succeeded in keeping a frog in the air, which is, as far as many times 7 goes into 56, naturally, the child prefers the bed.”

Think, parents, how much fun would it be if, at 6:30 p.m. on school nights, you could simply press a button, thereby activating giant magnetic shoes that would allow you to float upward, along with any frogs that happen to be in the house. Then, instead of yelling at the child, you could simply say, “FROG! STOP DRAWING! MARKING PEN ON THE WALL!”

Not so long ago, such use for magnetic shoes was considered impossible.

Dave Barry

LEVITY

FLOATING IN THE AIR

I am not making this up.

HUMANS could soon be so familiar with levitating scientists who perform such things that a single journalist wouldn’t even be able to relate it to a frog story. Instead, the child might simply ask, “What’s so special about floating frogs, anyway?”

So perhaps the story of the floating frog is not such an extraordinary tale. Perhaps it is worth treating the child to a story of the floating frog, instead of simply yelling at the child.

It’s all up in the air.
PERCEPTION CHANGE

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

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

in many textbooks
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)


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

Subatomic movements of domain walls
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
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%

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

change the number of electrons -> change conductivity
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

Chemically remove the substrate

Ultra-thin monocrystal

Would it be stable, or melt and oxidize?
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

dl little known about thin films of graphite
Dresselhauses' review 1981
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*

- graphite flakes on cellotape

*optical image*

**HOPG vs HDPG**
UNTIL A SINGLE LAYER FOUND

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

400 carbon atoms at 2000 K

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

THERMODYNAMIC STABILITY

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

- **nanosrolls**
  - Shioyama JMSL 2001
  - Kaner Science 2003

- **free growth**
  - Ebbessen (~60 layers)

- **substrate growth**
  - graphene on metal:
    - Land et al Surf Sci 1992
  - graphene on graphite:
      - J Phys 2002

as cited in our first paper in 2004
HISTORY OF GRAPHENE

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

cleavage
Kurtz *PRB* 1990
Ebbesen *Adv Mat* 1995

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

proof of isolated graphene

added along the same lines in our 2007 review

TEM

SEM

STM

AFM

LEED

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

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-
EUREKA MOMENT

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

width of a hair

50 µm

optical image

BEYOND OBSERVATION

50 µm optical image width of a hair

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 \(\sim 3\) layers 
on-off ratios \(\sim 30\) at room \(T\) and \(>100\) at low \(T\)

Electric Field Effect in Atomically 
Thin Carbon Films


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
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
Electric Field Effect in Atomically Thin Carbon Films

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Y. Zhang,¹ S. V. Dubonos,² I. V. Grigorieva,¹ A. A. Firsov²

Sergey Dubonos
microfabrication

Sergey Morozov
measurements

Irina Grigorieva
SEM, writing up

timeline finishes in mid 2004

Yuan Zhang
microfabrication

Da Jiang
graphene crystallites

Anatoly Firsov
microfabrication