'CLASSICAL' NANOSCIENCE: a Quick Survey

The term 'nanoscience' essentially refers to the length measure of 1 nanometre $(1 \text{ nm} = 10^{-9} \text{ m})$. This is 1000 times smaller than 1 micron = 1 μ m. To give some sense of scale, a grain of salt is typically 500 μ m across, a human hair is roughly 40-70 μ m thick, a typical bacterium may be 3-6 μ m long, but these are all huge compared to 1 nm, which is the scale of atoms and molecules (atoms are of order 0.1-0.3 nm in diameter, and small molecules containing 20-200 atoms may range in size from 0.6-1.5 nm in diameter). A typical bacterium is 3000-6000 nm long, and contains roughly a trillion (ie., 10^{12}) atoms.

Until the 1950's electronic devices were almost unknown outside a few research labs. The big changes came as the direct consequence of fundamental theoretical work done mainly in New Jersey, Moscow, and the UK. Theorists like Bardeen and Landau, in a few short years, gave for the first time a detailed understanding of metals, semiconductors, and superfluids. From that point it took only a few years for a bewildering array of new inventions to appear- transistors, solid-state lasers, superconducting devices, etc., which within only a decade had led to the new 'solid-state electronics' industry. However at that time it was very hard to miniaturize the new devices that were being built, and progress in miniaturization was slow. This is why it took another 35 years for the laptop to appear on the market.

Although there is a lot of talk at the moment about nanoscience and nanotechnology, in fact most currently available technology has yet to reach even the scale of microns. So we still have some time to think about how to deal with nanotechnology before it arrives in the supermarket. There are important differences between the situation prevailing in the 1950's and 2005. As noted above, the 'solid-state revolution' came primarily as the result of theoretical work. However nowadays the main thing driving the world towards nanotechnology is our new-found ability to 'nanofabricate', ie, to build pre-conceived structures at the atomic scale. It is important to understand that so far, almost all of this work has been on what I will call here '*classical nanoscience*'. This means that the nanosystems being constructed are operating classically, rather than using essentially quantum phenomena such as interference and tunneling (for which see the document on '*quantum nanoscience*'). The distinction is not always obvious, since the underlying behaviour of the individual particles in the nanosystems is certainly quantum-mechanical- this point is properly clarified in the separate document on Quantum Nanoscience.

Nanofabrication: The revolution in nanofabrication and nanomanipulation has come through the invention of new tools, such as the 'Scanning Tunneling Microscope', or STM. This is essentially a very sharp tip whose movement can be controlled with exquisite precision, and which can be used both to assemble structures at the atomic scale, and make incredibly high-resolution images of them (with resolution at scales far smaller than even the atomic scale). We begin by looking at some of these images, which give a foretaste of what sort of things nanoscience has to offer (NB: the STM is by no means the only nanofabrication tool- many others have now been developed)



Fig. 1: LEFT: Close-up of the tip of a "Scanning Tunneling Microscope" (STM) RIGHT: STM image of a Copper crystal surface- each 'hillock' is a Copper atom (Eigler et al, IBM)

Both the images and fabrication that have become possible in the last 10 years are quite spectacular. To illustrate this, I show some STM images, generated in the laboratories of Eigler (IBM) and Manoharan (Stanford). Above we see an image of a simple metal surface; and immediately below, images of some structures created using the STM- this is done by bringing the STM tip extremely close to the surface which is to be nanostructured, and then applying a reverse voltage to the tip so as to 'pick up' and drag different kinds of atom around to make the desired structures:



Fig. 2a: A circular "Quantum Corral" of magnetic Cobalt atoms on a Copper surface (Eigler et al., IBM)





Fig. 2b: LEFT: The Japanese word 'Kanji', or 'atom': Iron atoms on a Gold surface (Eigler et al., IBM) RIGHT: An elliptical corral of Nickel atoms on a Copper surface, with on extra atom inserted at an 'anti-focal' point (Manoharan et al., Stanford).

Note the astonishing precision of the patterned structures- which can be assembled in a few minutes by an experienced STM operator. The underlying surface (usually a Copper or Gold substrate) also shows fascinating features. There are complex 'wave patterns' generated on the surface by the presence of the nanostructure lying on top of them. This is a quantum effect- the electrons on the substrate surface are showing their wave-like behaviour, and we are seeing the scattering of these electron waves off atoms that have been placed on the surface, like ripples on a pond. Complicated interference patterns between the different scattered waves produce the patterns we see here. The most dramatic interference is seen in the circular corral, where waves scattering inwards from the circular walls all meet together in the centre.

These results seem really extraordinary to many- one gets the impression that at some point in the not too distant future, making nanostructures will be like assembling lego toys. However, nanotechnology will require much more than just the ability to make small nanostructures. To actually *use* these structures will require both important technical advances, and a new theoretical framework. The technical advances will include (i) reliable and repeatable nanostructuring- many of the uses imagined for nanostructures require the nanocomponents (molecules, nanotubes, very small metallic wires, rings, etc) to be free of any defects or impurities, and completely reproducible; and (ii) very sensitive 'read-in' and 'read-out' connections between the nanostructure, we can control them and probe them. Both of these pose interesting and difficult challenges for experimental nanoscientists, but few doubt that they will be solved. To see why this is, we now take a 'bird's eye' look at some of the most important current developments.

1.1: MAKING THINGS SMALLER in CLASSICAL NANOSCIENCE

Many current ideas in nanoscience simply involve much smaller versions of already existing devices. One example, involving currents passing through a single molecule, was recently published by Park et al.- it incorporates a single molecule into a standard transistor design, to make a 'nanotransistor':



Fig. 3: A 'molecular transistor' (from Park et al.)

Another example of the same miniaturization is the 'quantum dot', which relies on the quantummechanical Pauli exclusion principle to put just a few electrons into a very small region (the nanofabricated 'dot'). Essentially one creates an artificial atom, with external control over the number and energy of the electrons, using electric and magnetic fields.



Fig. 4: LEFT: A set of electronic reservoirs ('dots' or 'holding pens') and gates between them- a primitive quantum dot array (from Folk, Marcus, et al., UBC, MIT and Harvard). RIGHT: Two SET's (Single electron transistors') coupled so that electrons can be transferred between them (R. Clark, Sydney; the whole platform shown is 600 nm across)

One can also transfer electrons between dots, using small externally controlled voltages, thereby making nanocircuits involving just a few electrons (instead of the huge number involved in contemporary microcircuitry). Note that the circuits shown in the pictures are still hundreds of nanometers, or even several microns, in size- but this scale is being continually reduced.

Nanotechnology will not just be about electrons moving through circuits. Information has for many years been transmitted using electromagnetic waves, either using old-fashioned radio- and micro-waves, or in more recent technology, using much shorter wavelength light waves in optical fibres. The natural

progression here is towards what are called 'photonic' devices, in which light is channeled through microscopic tubes or lattices of tubes- this is now a topic of active research:



Fig. 5: A 'photonic band-gap' structure, used for channeling light (S John et al., Univ of Toronto); note scale in microns.

Another kind of miniaturization involves magnetic phenomena. At the most microscopic scale, magnetism comes from what is called '*spin*'; this is a quantum-mechanical property of all elementary particles, including electrons and nuclear particles. The spin behaves as though a tiny electric current was circulating, and this produces a small magnetic field in the direction of the spin axis. When all the spins in a solid line up together we get a large field- this is a ferromagnet. The tiny magnets which make up the memory elements of a modern hard disc are no larger than a bacterium, but they still contain trillions of electronic spins, and the tiny magnetic fields produced by spin each add together to produce a field which can be sensed by a hard disc reader. Modern research in '*spintronics*' is pushing the size of these magnetic components to ever smaller scales, and also using newly-discovered effects like 'colossal magnetoresistance' to manipulate spin current flows at the nanoscale (to produce, eg., currents involving only spins of one orientation). These apparently mundane developments are of enormous practical importance- the hard disc industry alone is presently worth ~ \$350 billion per annum worldwide.



Fig 6: Spintronics. LEFT: a spin valve scheme- only 'up' spins can pass through it. RIGHT: electron microscope image of a double spin valve, made from (GaMn)As (note scale)

One should not assume that these new developments are exclusively the preserve of physicists. Many of the key new ideas are now emerging at the nexus between physics, chemistry, and biology, and so the line between these subjects is fast disappearing in nanoscience. Key elements in this new synthesis are carbon nanotubes, arrays of small organic molecules, and biological chain molecules like DNA, made by chemists like J Polanyi (Toronto) and R Smalley (Houston).



Fig. 7: The tip of a nanotube, made from a lattice of Carbon hexagons- the nanotube is roughly 1 nm in diameter, but can be mm or cm in length.

Nanotubes, organic molecules, and DNA chains are genuinely nanoscopic in size- unlike the structures so far made by physical nanostructuring methods, which are still hundreds of nm in size. Nanotubes are very thin (less than 1 nm in diameter) but extremely long (in some case many microns in length), made from carbon- they can be made to conduct, and one can also attach molecules to them, or even small molecules or chains of molecules inside them. Molecular biologists are just beginning to use nanofabrication and nano-manipulation techniques to make changes to DNA chains, by substituting or attaching atoms or molecules to them, and using nanoprobes to investigate the results. Teams involving physicists, chemists, and biologists are making 'cages', using the unraveled strands of DNA molecules as the cage superstructure, and inserting pre-made molecules inside these, to produce 3-dimensional ordered arrays of these molecules.



Fig. 8: Segment of DNA chain (blue), into which transition metal complexes (orange) are inserted (J.Barton et al., Caltech)

Both nanotubes and DNA chains are very strong and can be made incredibly long, many microns or even cm in length (ie., tens of millions times longer than their diameter of 1 nm). They form backbones or even conducting wires into which all sorts of chemical groups can be inserted, for use in almost every imaginable kind of structure. The ideas for this range from purely mechanical objects such as 'nanogears' or 'nanoropes' (probably impractical), to much more sophisticated 'designer drug' delivery systems (probably of enormous future importance). Here are some examples:



Fig 9: *LEFT: a cross-cut through a 'nanorope' made from c. 100 nanotubes (Smalley, Houston) RIGHT: structure of a 'nanogear' made by inserting small side-groups into 2 parallel nanotubes*



Fig. 10: Designer drug delivery, by insertion of molecular sidegroups into DNA strands (Barton et al, Caltech)

The importance of possibilities in future 'designer drug' and genetic delivery is indeed hard to overestimate. Other ways of delivering these that have been suggested include the use of designed 'nanoplatforms', with on-board therapeutics and sensors, designed to target diseased cells, or to do gene therapy using, eg., protein coatings from viruses. Nanoscientists and economists like to talk about '*convergence*', which is supposed to refer to the way in which different technologies come together to produce a vast leap in our understanding and capabilities- one of the most widely-discussed examples of convergence is that of biotech and nanoscience (including both nanoprobe and delivery systems), and enhanced communication and control using nanocommunication information technology.

Finally, one can use molecules in conjunction with engineered electronic structures, to make remarkable hybrids. For example, conducting nanotubes and DNA chains connected to fabricated electronic structures have been used to make very small electric circuits, which really do approach the nanoscale:



Fig. 11: LEFT: Electrical contacts between 2 Gold electrodes made using a short DNA chain segment RIGHT: image of a 'nanoring', made from a Carbon nanotube, incorporated into a sub-micron Transistor (NASA). The diameter of the ring is ~100 nm.

All of this discussion of current efforts in nanoscience would not be complete without mentioning the crucial role of new materials. The last 20-30 years have seen a quiet revolution in our theoretical understanding of complex materials, both inorganic and organic, which has transformed both theoretical chemistry and solid-state physics. Models such as the Anderson and ZSA models, along with very powerful numerical methods such as the "LDA" or "LDA + U" methods, have now finally made it possible to attempt a "bottom up" approach to complicated molecules and new composite materials. What this means in practice is "designer molecules" and new "designer quantum materials". The natural area for all of this is the nanoscale.

So far this has design process has hardly started. The most striking successes so far have been the design of structures based around nanotubes and DNA molecules, of Quantum Dot-based structures, or structures on surfaces, including novel molecular structures or very small structures like the Quantum Corral; and the design of a variety of nanoparticles (crystalline or otherwise) with interesting properties, many of which depend on the peculiarities of electronic structure near surfaces. However in the longer term, it is clear that these new ideas will have a huge influence on the development of nanoscience. Probably the most promising area for striking new developments is in the new area of 'quantum materials'. This brings us inevitably to the most unpredictable part of nanoscience, that depending in an essential way on quantum mechanics. This discussed in the separate document on *Quantum Nanoscience*.

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