

CONDENSED MATTER: the SOLID STATE

We learned in the last few sections about the great mysteries of the universe & how it is made. We now turn to a discussion of the collective properties of matter, bewildering in their variety – ranging from simple atoms to the overwhelming complexity of living systems. The energy range over which matter can exist in condensed (ie., solid or liquid) form is enormous – up 10^{10} K in the centre of neutron stars. Thus most matter in the universe is condensed.

One of the miracles that we want to understand is – how is it that so much order & structure has emerged since the universe began? How is it that an inanimate universe governed by simple laws could have generated such complexity (including life)?

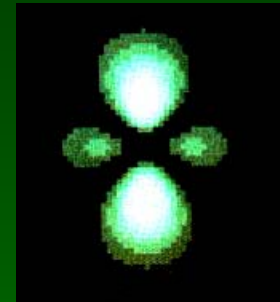
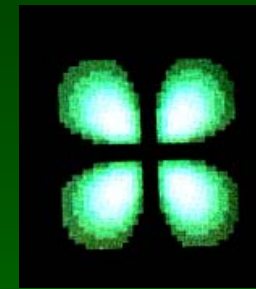
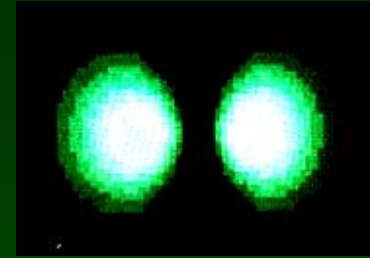
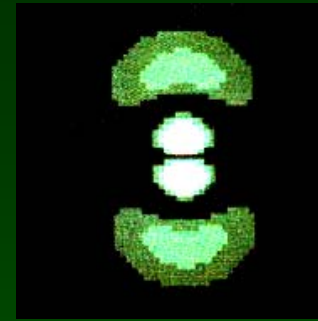
We begin our story by looking at HARD MATTER - the solid state. Solids exist because of bonds that can form between atoms (or at very high pressures, between nucleons). These bonds are entirely a result of quantum mechanics. The almost limitless structures that form in Nature result from the directionality of these bonds, & from various quantum coherence effects between groups of atoms.

Solid-state physics has been central to high-tech for over 60 years. In recent years our ability to manipulate and control the structure of materials at the molecular scale has led to new nanotechnologies

ATOMIC STRUCTURE: The Elements

With the discovery of Quantum Mechanics the old dream of Democritus was realised- the existence & structure of atoms is an immediate consequence of the quantum rules, for electrons moving in the field of the nucleus. Different atomic 'shapes' come from the different shaped electron clouds, having 'lobes' (called 'atomic orbitals') of increased probability in certain directions.

Orange	Metals
Light Green	Metalloids
Cyan	Non-metals
Yellow	Transition Metals
Pink	Gases



Above: Some of the electronic states in an atom. We see the probability density for one electron, for 4 different states.

The periodic table of the elements

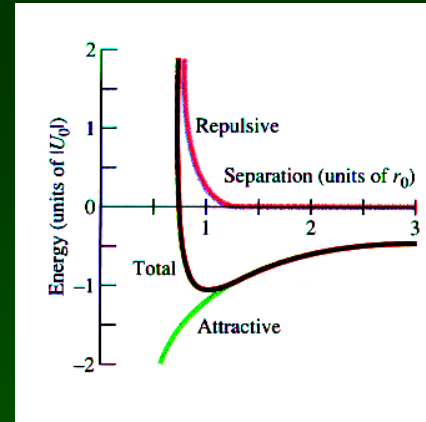
	1A	2A	3A	4A	5A	6A	7A	8	1B	2B	3B	4B	5B	6B	7B	0		
1	H															He		
2	Li	Be									B	C	N	O	F	Ne		
3	Na	Mg									Al	Si	P	S	Cl	Ar		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	A															
	L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
	A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

How then do we get elements? Pauli exclusion – no 2 electrons can occupy the same state, so each set of 'lobes' fills up, & when all are full, the atom begins filling a new 'shell' of similar orbitals further from the nucleus. Thus we get a 'repeating pattern' of atoms, depicted in the periodic table. 2 elements in the same vertical column have the same set of occupied outer orbitals, & hence similar chemical properties

THE CHEMICAL BOND: Sharing of electrons

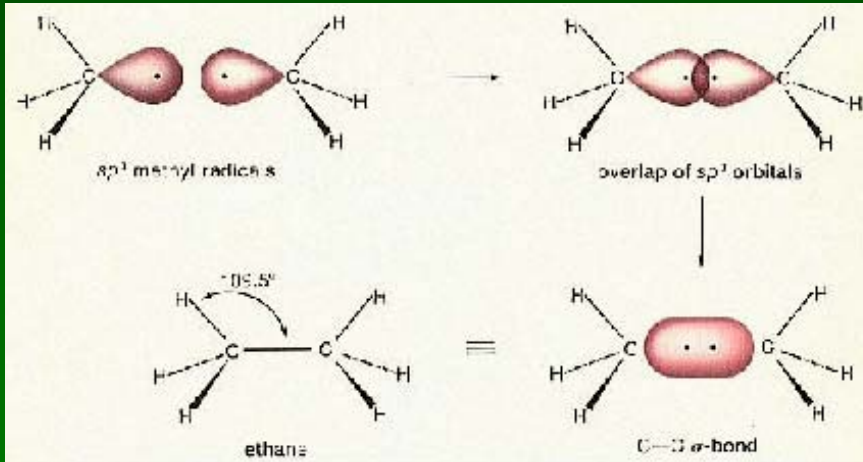
Quantum Mechanics explains chemical bonding. As we saw, in QM we can form states which are superpositions (ie., sums) of different states- allowing them to spread in space, which lowers their kinetic energy (this is clear from the uncertainty principle).

Electrons then spread between atoms by tunneling, & lower their energy. Chemical bonding is just this quantum-mechanical sharing of electrons. The electron wave-functions 'lobes' come off the atoms in



interaction energy
between 2 atoms.

certain directions- these are the bond directions. Note- the electron clouds repel each other at short distances, because of the exclusion principle, which stops electron states from overlapping in space (they also repel each other when they are further apart, because of the Coulomb interaction between like charges). These repulsions are what make matter HARD.



A covalent 'sigma' chemical bond, in ethane (C_2H_6).

We can put some numbers to this, in a nice illustration of the uncertainty principle. Suppose we have an electron of mass m , and its wave-function increases its spread from r to R . What are the kinetic energies of these 2 states? According to the uncertainty principle we have

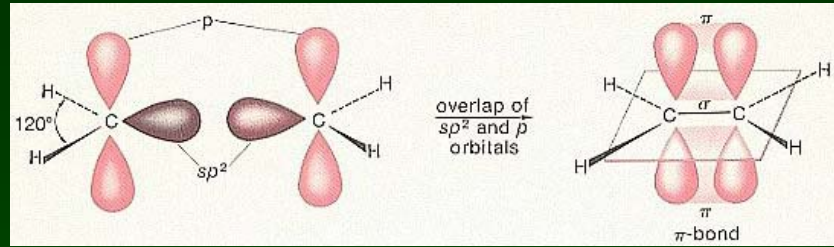
Energy before spreading: $E_r = \frac{h^2}{2mr^2}$

Energy after spreading: $E_R = \frac{h^2}{2mR^2}$

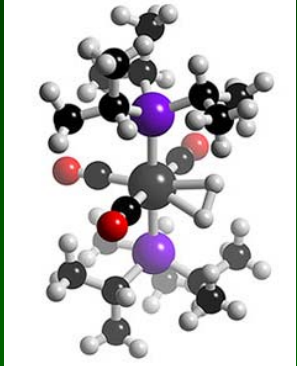
Because $R > r$, the electron lowers its energy by spreading out – it is then SHARED between the atoms.

CONDENSED MATTER: BONDS → MOLECULES

Chemical bonds lead to an amazing array of structures. Only the noble gases (He, Ne, Ar, etc.) find it hard to bond with other atoms – their shells are already full.



Formation of ethylene (C_2H_4) via sigma- and pi-bonding

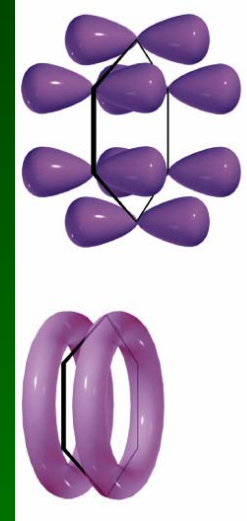


A tungsten-based molecular complex

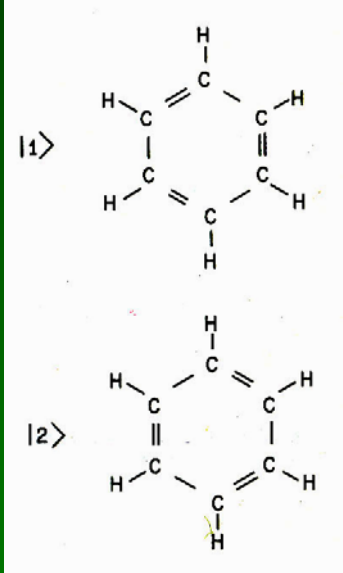
Almost any structure can be formed but most of them are not stable. On earth, both in Nature and in industry, metallic complexes (metals bonded with lighter elements) are very important. Many of them play a key role in living organisms – others are highly poisonous. Most of them dissociate in water (ie., they dissolve)

By far the most complex structures are formed by carbon bonds – these are very strong & so huge molecular structures can form with them. The covalent sharing of electrons between C atoms can take various geometries, depending on which orbitals overlap to share electrons (the most common are 'sigma' and 'pi' bonds). One can also have quantum-mechanical superposition of different bond arrangements, as in benzene.

Hence the subject of 'Organic Chemistry' (the chemistry of C-based molecules). The chemistry of molecules involving C rings is called 'aromatic chemistry', with some v important players (see Figs.).



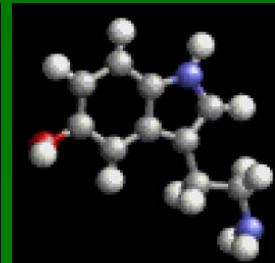
The benzene molecule forms 'pi-bonds' (left), with a QM superposition of the 2 states shown above right



The C-60 molecule (the 'buckyball')

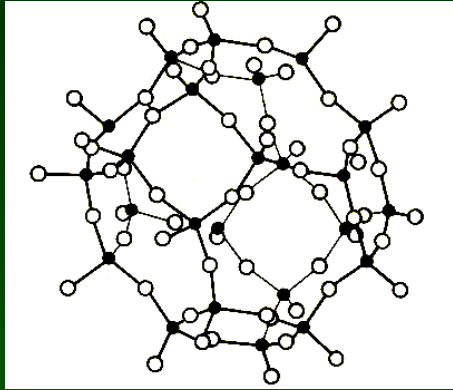


Caffeine



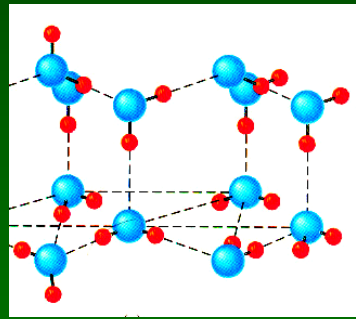
Serotonin

CONDENSED MATTER: Crystals



Obviously one can make repetitive patterns by assembling many atoms of the same kind.

Hundreds of different basic patterns are possible, giving a large variety of natural crystals made from different atomic sub-units. Their strength and



TOP: The basic 'unit cell' structure, of Si & O atoms, repeated in quartz.

BOTTOM: structure of water ice, made from H₂O units.

hardness depends entirely on that of the bonds between the atoms. Thus diamond is very hard (depending on strong inter-Carbon bonds), but graphite is made from Carbon planes which are only weakly coupled to each other- so they easily slide across one another. One can convert graphite to diamond by applying pressure & heat, & make many other Carbon-based structures (eg. the 'buckyball', C-60, on page 5.41). One can also make 'molecular crystals' of molecules, held together by weaker bonds between the molecules.



Iron pyrite (FeS) ; 'fool's gold'.



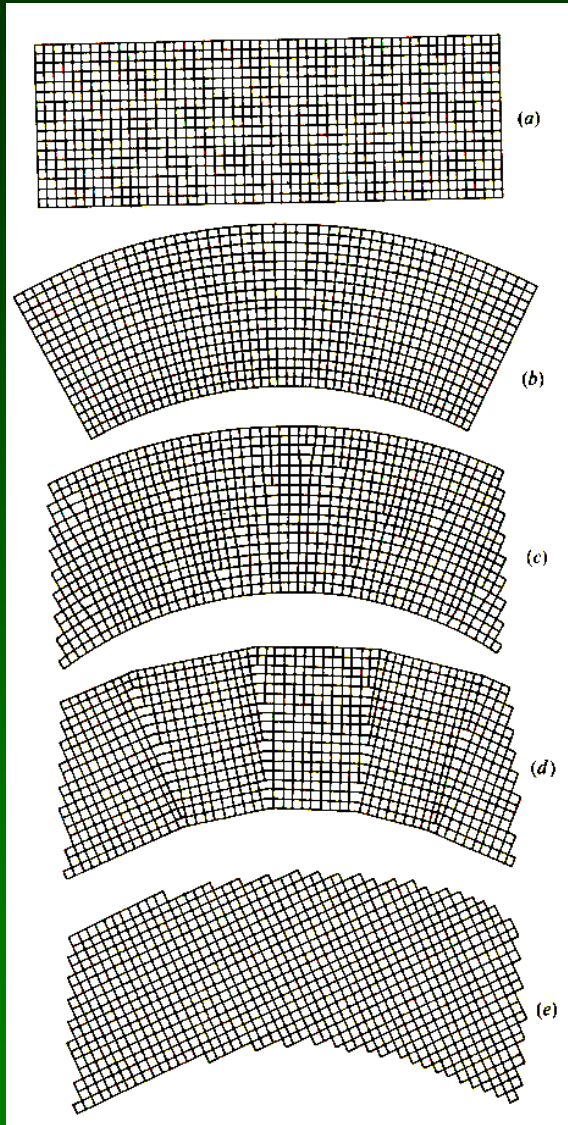
Haematite crystals (Fe₂O₃)



Epsomite crystals

It is rare in Nature to find large crystals – but we are surrounded by aggregates of different microcrystals. These polycrystalline amalgams are known as rocks.

CONDENSED MATTER: Structure of 'Hard' Solids



Bending a crystal creates 'fault lines' (defects, dislocations), & then polycrystals. Heating then anneals out the dislocations.

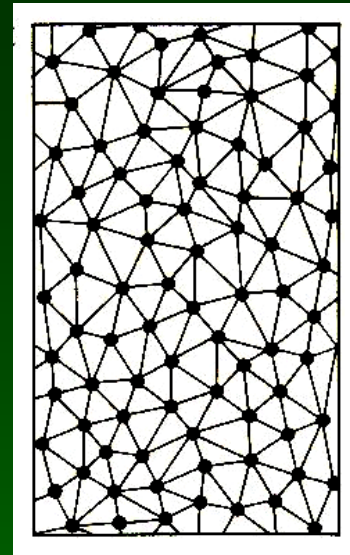
Most hard objects are not macroscopic crystals! At the microscopic level we have many kinds of structure. For example:

(i) Many microcrystals, which fit together, with dislocations & defects between them. Heating a 'polycrystal' 'anneals' it- the defects move out, leaving a single crystal. Defects are formed when a crystal is strongly strained.

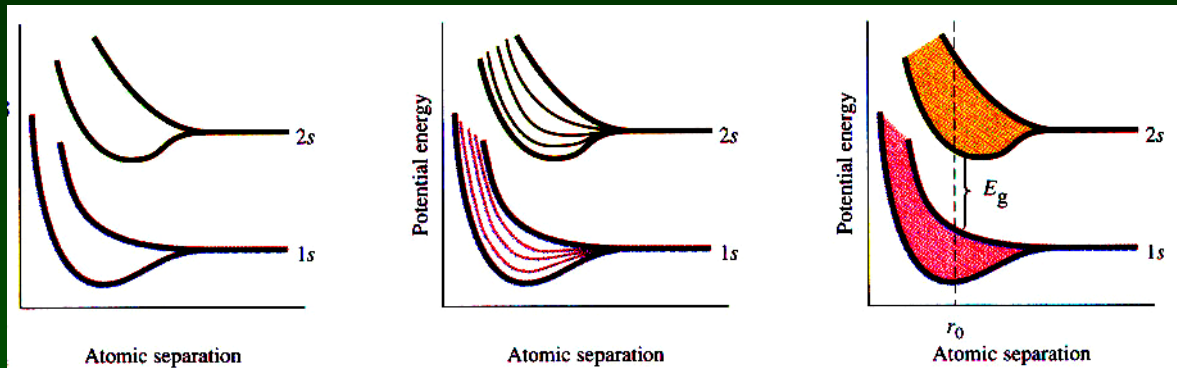
(ii) We can have defects everywhere, with atomic bonds oriented in random directions. The system has to melt to get rid of such extensive disorder. Such systems, called 'glasses' (eg., window glass), form if a crystal solidifies too fast. One can freeze defects by adding impurities, preventing plastic deformation, & making the material strong- eg. steel.

(iii) One can have 'Quantum Solids', in which the atoms or defects can tunnel quite rapidly. These solids can still change their configurations even at absolute zero.

However by far the most complex solids are those formed by assembling large molecules together, making 'soft matter' - see next section



The atomic structure of a glass



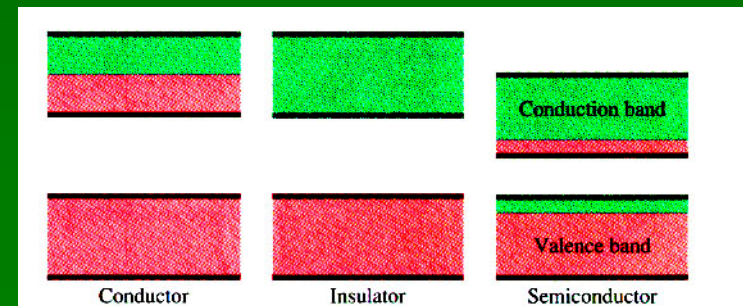
LEFT: The energy levels of 2 atoms as they approach.
CENTRE: The levels of 5 atoms forced to approach each other.
RIGHT: The levels of very many atoms approaching each other.

What stops the electrons in a solid from spreading over the whole solid? As they spread, electron clouds start to overlap, & 2 things happen:

(i) electrons are forced into different states by the Pauli principle – stopping them from overlapping too much in space.

(ii) electrons that get too close to each other repel each other – the Coulomb repulsion between like charges. This also stops them from closely overlapping in space.

We can now understand the difference between metals (where electrons spread over the whole system in delocalised states- so metals conduct electricity), & insulators (where electrons are bound to the atoms). In metals the electrons do spread out, but to avoid each other they go into wave-like states with different wavelengths & energies – the set of all these states & their different energies is called an 'energy band'. If an energy band is only partly full, then it is easy to move electrons from one state to another, and we have a conductor. In insulators, electrons can only move by jumping from localised atomic states to a higher energy band, which takes a lot of energy.



The filling of states up to the Fermi energy in 2 bands of a conductor, insulator, & semiconductor. Filled states are in red, empty ones in green.

SOLID-STATE ELECTRONICS

In modern times a technology of 'quantum devices' has developed, depending on our understanding of electron states in solids.

The first major development was the transistor, & now we have thousands of devices ranging from solid-state lasers to electronic computers. Computers work by transferring electrons around- to make them faster one needs smaller components.



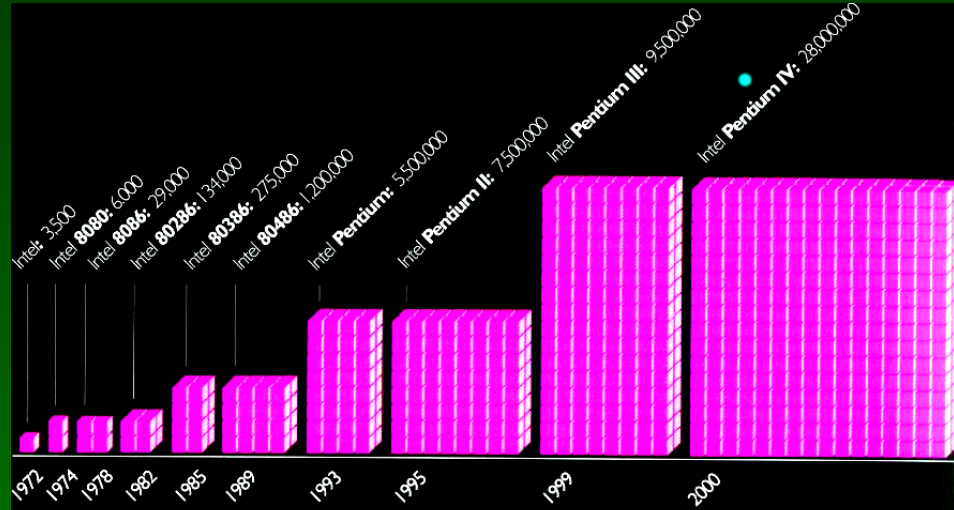
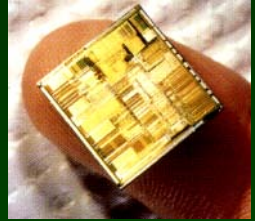
1st transistor (1949)



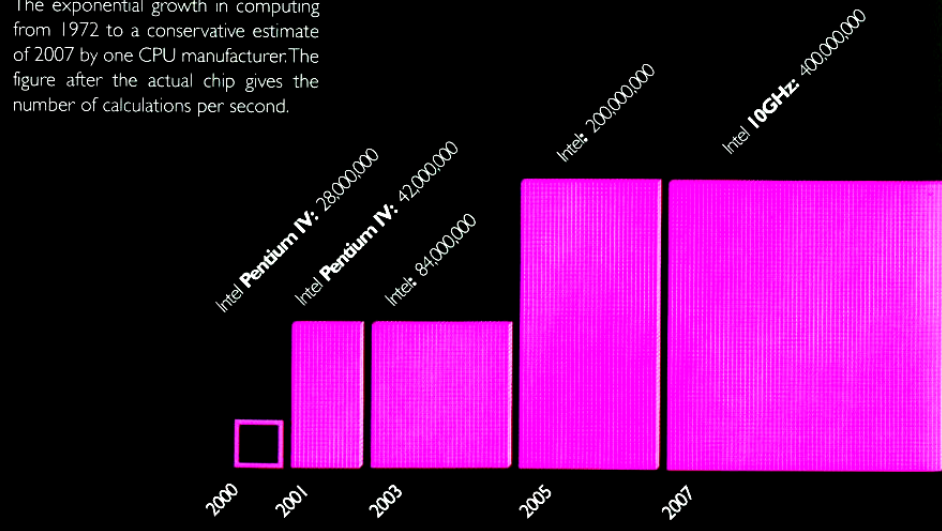
Oppenheimer, von Neumann, & the Los Alamos computer

Computing history is a story of component size reduction- which still has far to go.

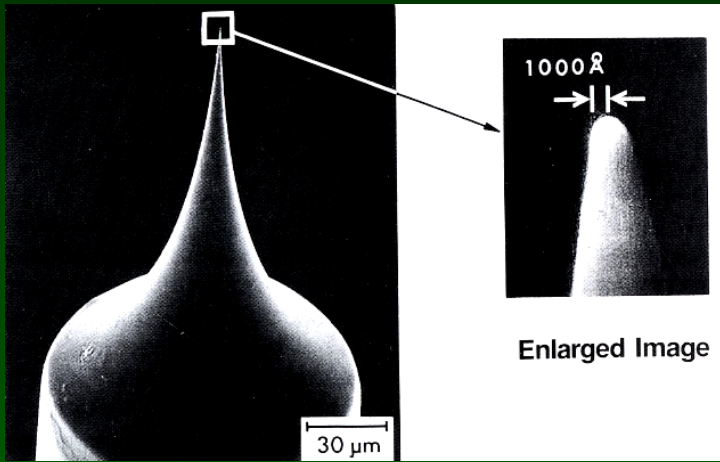
RIGHT: a Pentium 2 chip, containing 5 million processing elements
BELOW: rise in computing speed, 1972-2007



The exponential growth in computing from 1972 to a conservative estimate of 2007 by one CPU manufacturer. The figure after the actual chip gives the number of calculations per second.

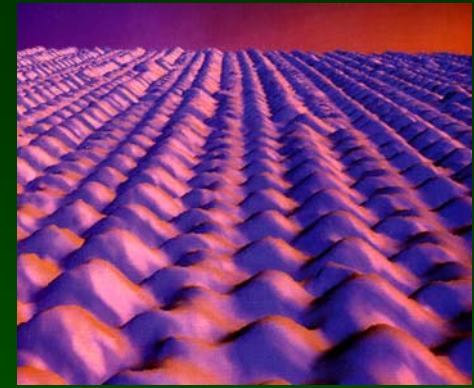


CONDENSED MATTER: Solid Surfaces



STM tip (human hair ~ 100 μm thick)

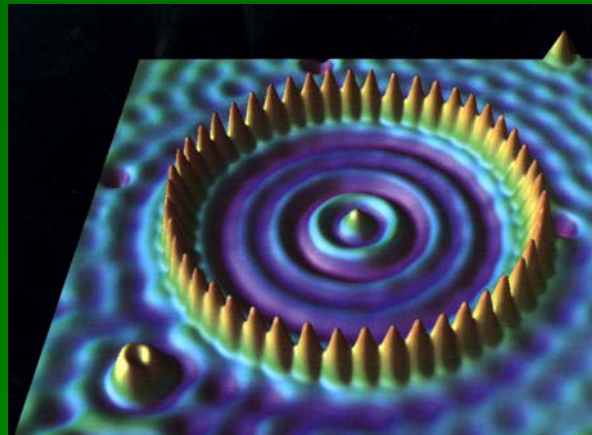
In the last 20 yrs a new technique has allowed physicists to look at & manipulate matter at the atomic scale on solid surfaces. The STM (Scanning Tunneling Microscope) is a very sharp needle which moves across a surface, only a few Angstroms



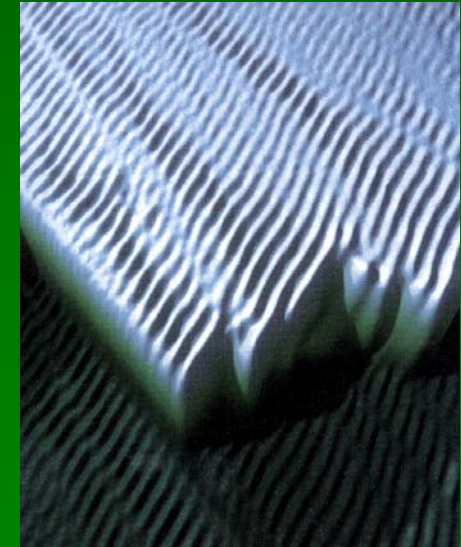
Surface of Cu using STM

above it. Electrons quantum tunnel between the two, & by measuring the electric current we look directly at the electronic clouds on the surface.

One sees not only the structure of the electrons localised around atoms, but also the wavelike patterns of itinerant electrons moving across the surface.. The STM's can also be used to drag or pick up atoms, to make surface structures- such as the famous 'quantum corral'. The STM is one of the important tools used in the modern technology of 'nanoscience', ie, making nm-sized structures.



A 'quantum corral', with Co atoms on a Cu surface.



Surface of Be, near an atomic 'edge'.

The Scale of Things – Nanometers and More

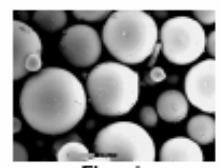
Things Natural



Dust mite
200 μm



Ant
~ 5 mm

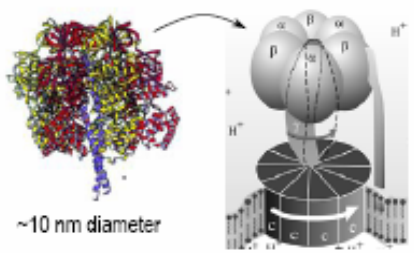
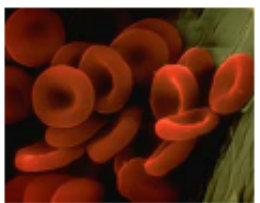


Fly ash
~ 10-20 μm



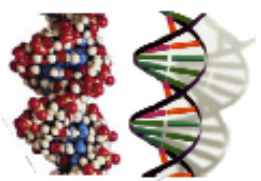
Human hair
~ 60-120 μm wide

Red blood cells
(~7-8 μm)

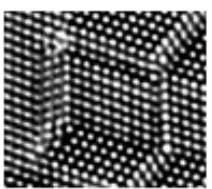


~10 nm diameter

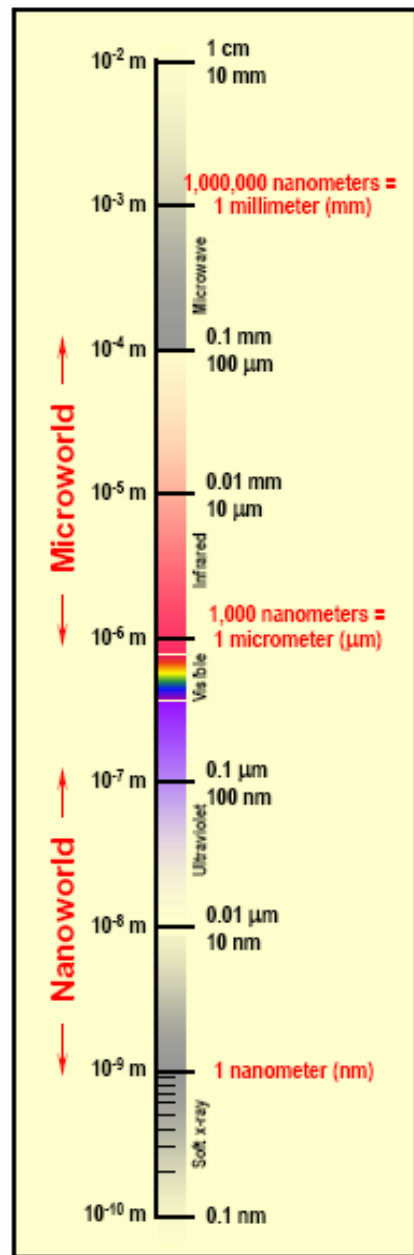
ATP synthase



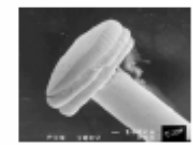
DNA
~2-1/2 nm diameter



Atoms of silicon
spacing ~tenths of nm



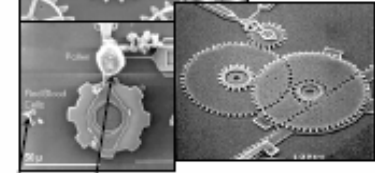
Things Manmade



Head of a pin
1-2 mm

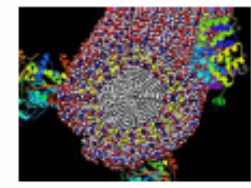
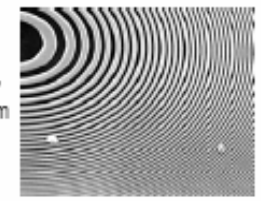


MicroElectroMechanical (MEMS) devices
10 -100 μm wide

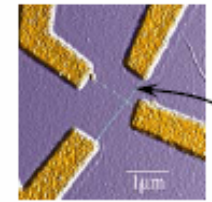


Pollen grain
Red blood cells

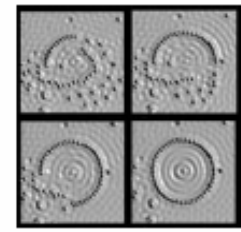
Zone plate x-ray "lens"
Outer ring spacing ~35 nm



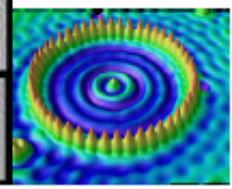
Self-assembled, Nature-inspired structure
Many 10s of nm



Nanotube electrode

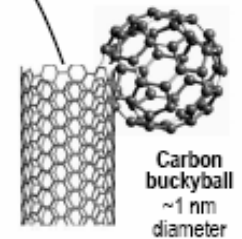


Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm



The Challenge

Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.



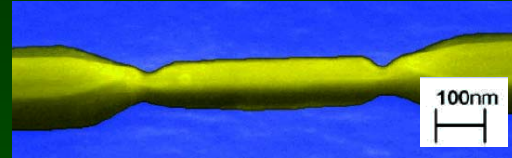
Carbon buckyball
~1 nm diameter

Carbon nanotube
~1.3 nm diameter

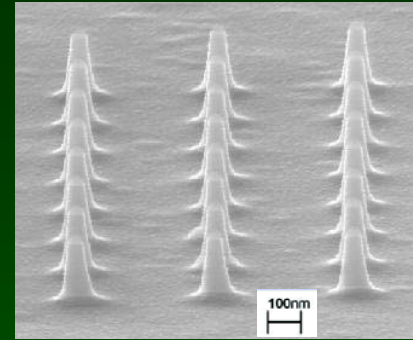
NANOSCIENCE: New Quantum Structures

The new techniques of 'nanofabrication' are one of the main factors behind nanoscience. It is likely that in the next 20-30 yrs this will revolutionise large parts of technology.

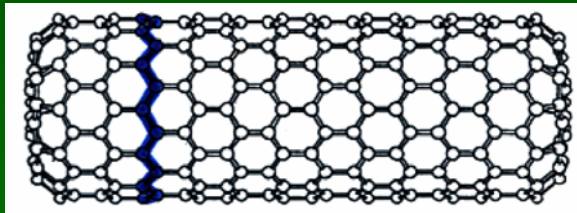
The nanoscale is defined by the nanometer; 1 nm is 10^{-9} m. An idea of different length scales appears on the previous page (recall that 1 Angstrom = 0.1 nm is the size of a small atom). Using the techniques of nanofabrication it is now possible to make structures down to the atomic scale. These techniques are called 'top-down' nanoengineering tools – controlled by us.



nanofabricated Au wire



semiconductor Nanotowers

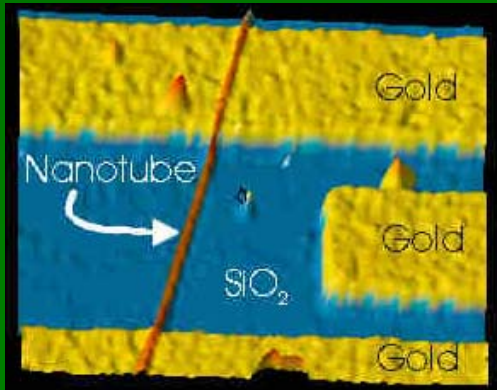


ABOVE: A Carbon nanotube capped at both ends by buckyball sections. The diameter is roughly 1 nm

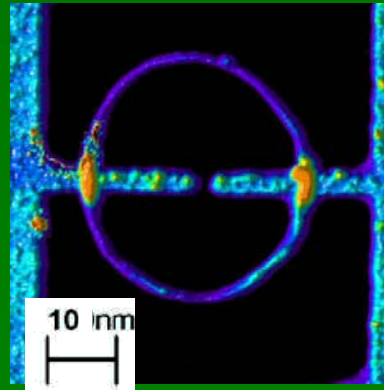


Cross-section of Aacarbon nanotube

At scales of 10-100 nm one can make structures by 'electron beam lithography', using very fine beams of high-energy electrons to cut metals & semiconductors into specific shapes. One can Make nanoelectronic circuits with these – more recently these circuits have been connected using 'Carbon nanotubes', which are only 1 nm in diameter, but extremely strong – they can be made mm in length.

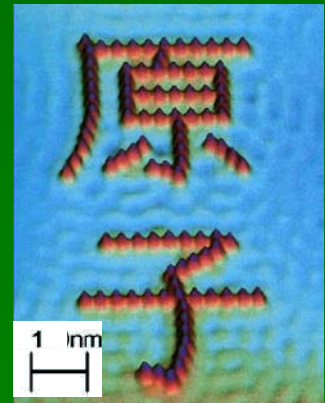


Nanotube on Au alectrodes



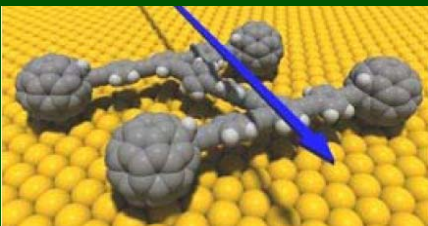
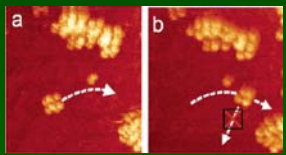
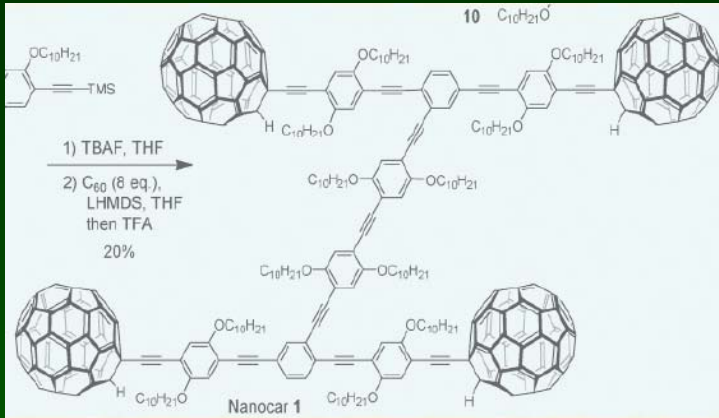
Nanotube on Au alectrodes

Using STM's, one can make Atomic size structures – as seen at right.



'Kenji' (Japanese for atom) written with Co atoms on Cu

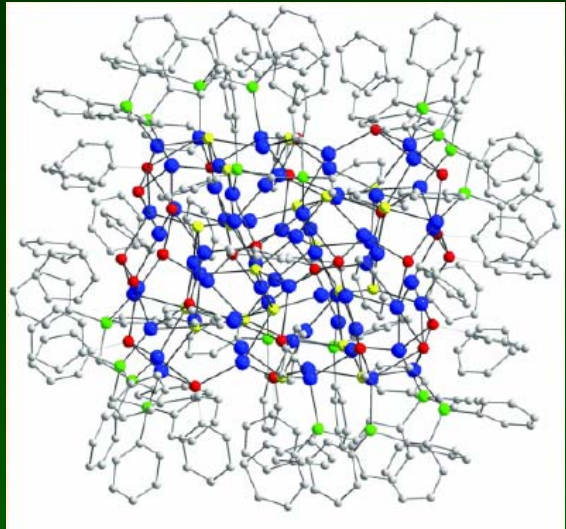
NANOSCIENCE: Molecular Engineering



A 'nanocar' with chemical makeup shown at top. It can roll across a gold surface – STM experiments can track its motion

Another approach to design of nanosystems is 'bottom-up', ie., starting with existing nanoscale objects.

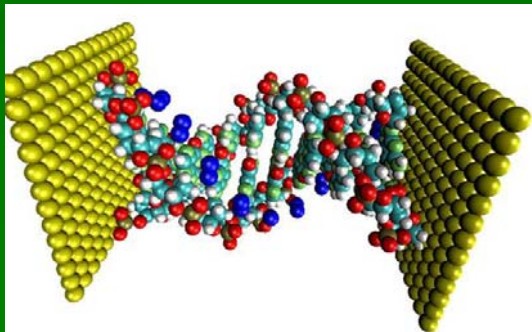
Such objects are typically molecular, and instead of being made by man using top-down methods, they are the product of chemistry.



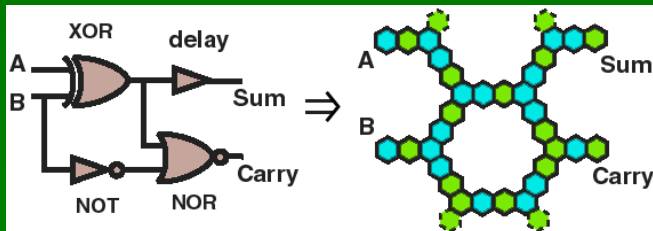
Metallic cluster molecule, with Au:Pd core

The simplest such molecules have metallic cores, and can be assembled in many ways. Currently they are used where pinpoint delivery of the metals is required (eg., for medical applications).

A much greater range of applications is envisaged for organic molecules. These can range from the quite bizarre (such as nanoscale mechanical devices – the nanocar shown above is an example), to possible molecular electronics devices. A major discovery of the 1980's was of conducting organic molecules – in principle this opens the way to electronic circuitry at the nanoscale level, using conducting polymer chains as quantum wires.



DNA chain connecting 2 Au electrodes



Gating circuit using aromatic chain structure

Some of the possibilities now being discussed are shown here. Note that to make these is hard, & needs 'top-down' approaches