

Nanomanufacturing

University of Michigan

ME599-002 | Winter 2010



01: Taxonomy and geometry of nanostructures

January 11, 2010

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Announcements



- Please fill out the info sheet if you are new
- Enrollment limit raised –overrides not needed
- If you're not on the ctools site (ME599-002), tell me and I will add you

- Prerequisites and grading
- Literature review → topic summary report, details TBA

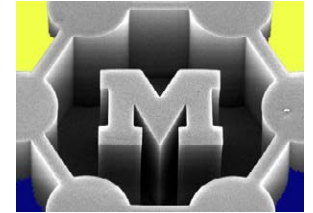
- Literature searching/archiving –extra session?

Today's agenda

- Classification (taxonomy) of nanoscale structures
- Examples of scaling: surface area and surface stress
- Nanoclusters: magic numbers
- Structure of carbon nanotubes (CNTs)



Today's readings



Nominal: (on ctools)

- Teo and Sloane, **Magic Numbers in Polygonal and Polyhedral Clusters** –need to know concepts only
- Charlier, **Structure of Carbon Nanotubes** –will use it on PS1
- Atomistix, **Periodic Table of Carbon Nanotubes** –for reference

Extras: (on ctools)

- Roduner, excerpt on **Bulk and Interface**
- Park, **Types of Nanomaterials** (section 3)
- Smalley, **Great Balls of Carbon**

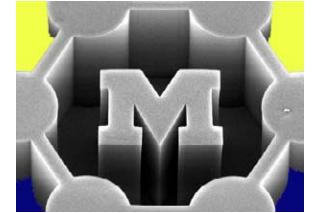
Background for today:

- Crystal structures:
http://en.wikipedia.org/wiki/Crystal_structure
- Vector math: dot products, cross products

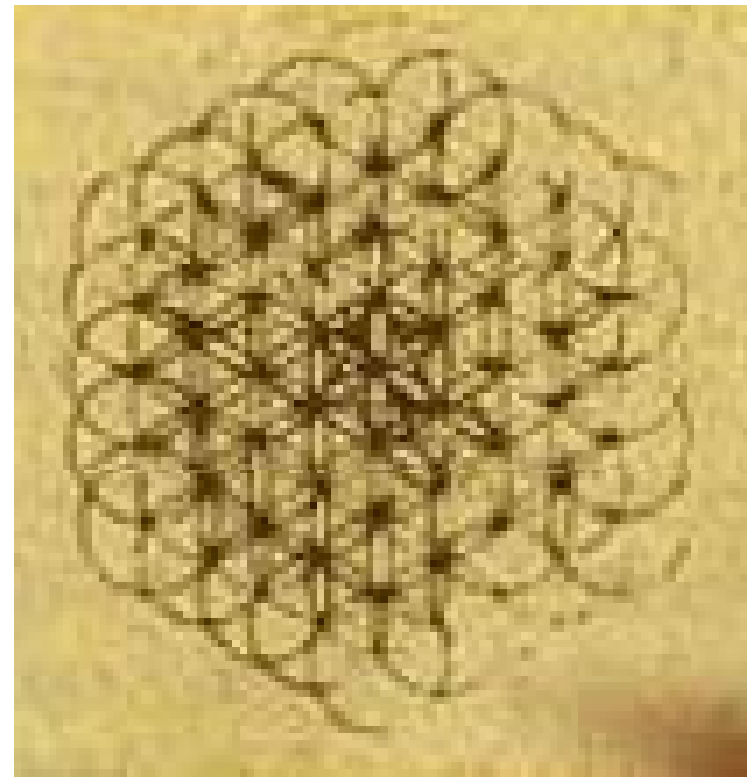


Shibuya district, Tokyo, July 2006

Circles from history: building structures from a plane

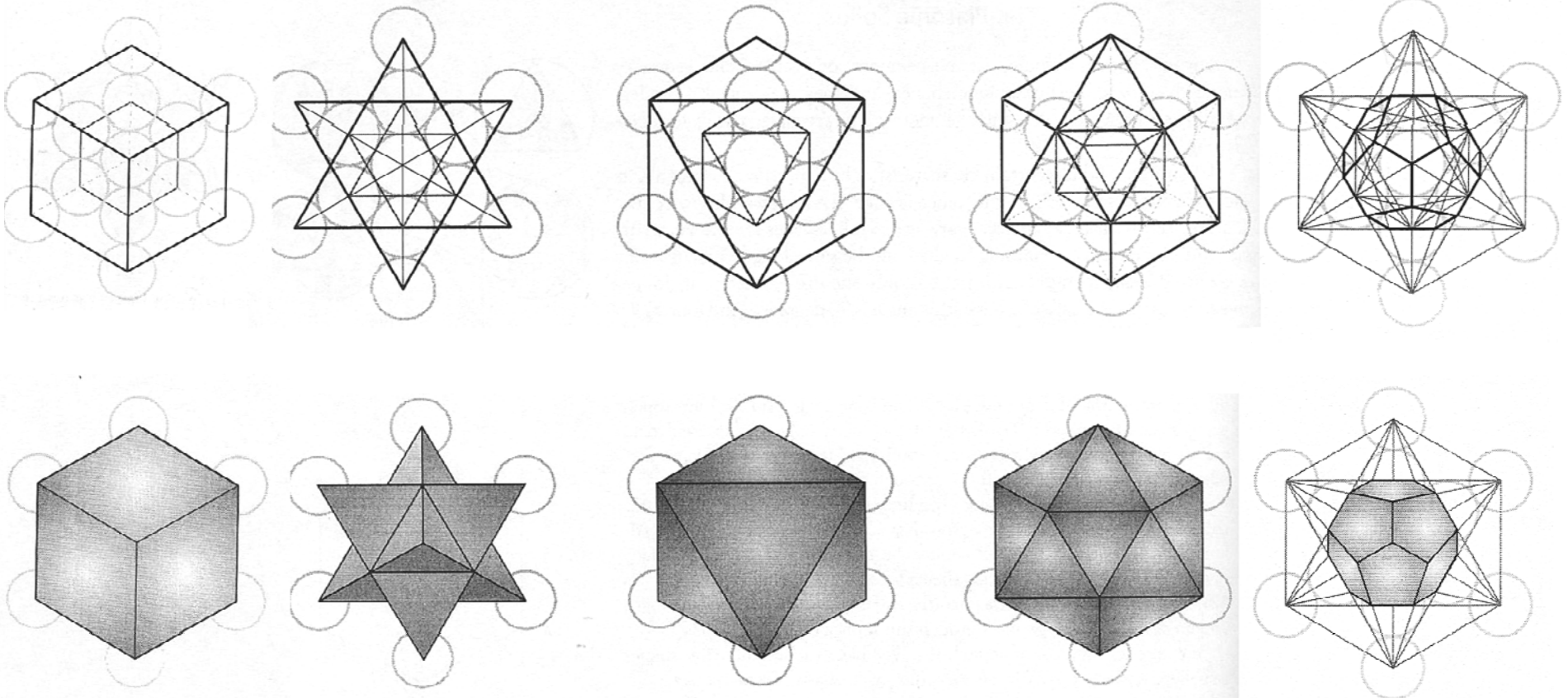
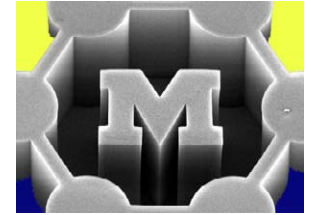


Osirian temple in Abydos Egypt, c.2000 BC



Leonardo DaVinci, c.1498 AD

The platonic solids



Cube	Star Tetrahedron	Octahedron
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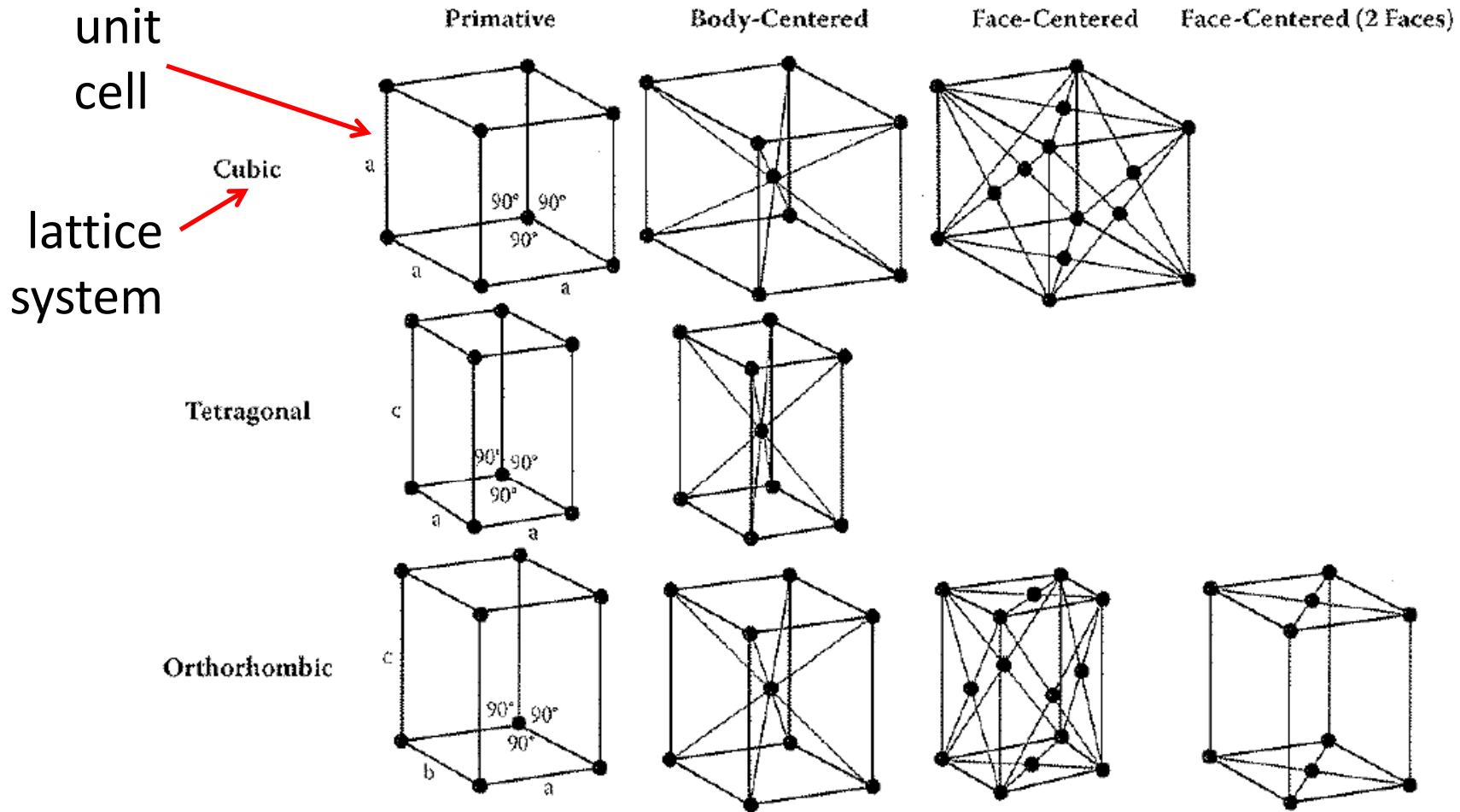
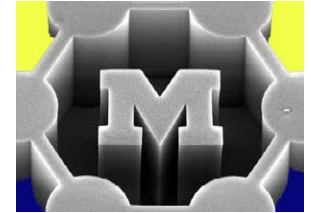
Icosahedron

Dodecahedron

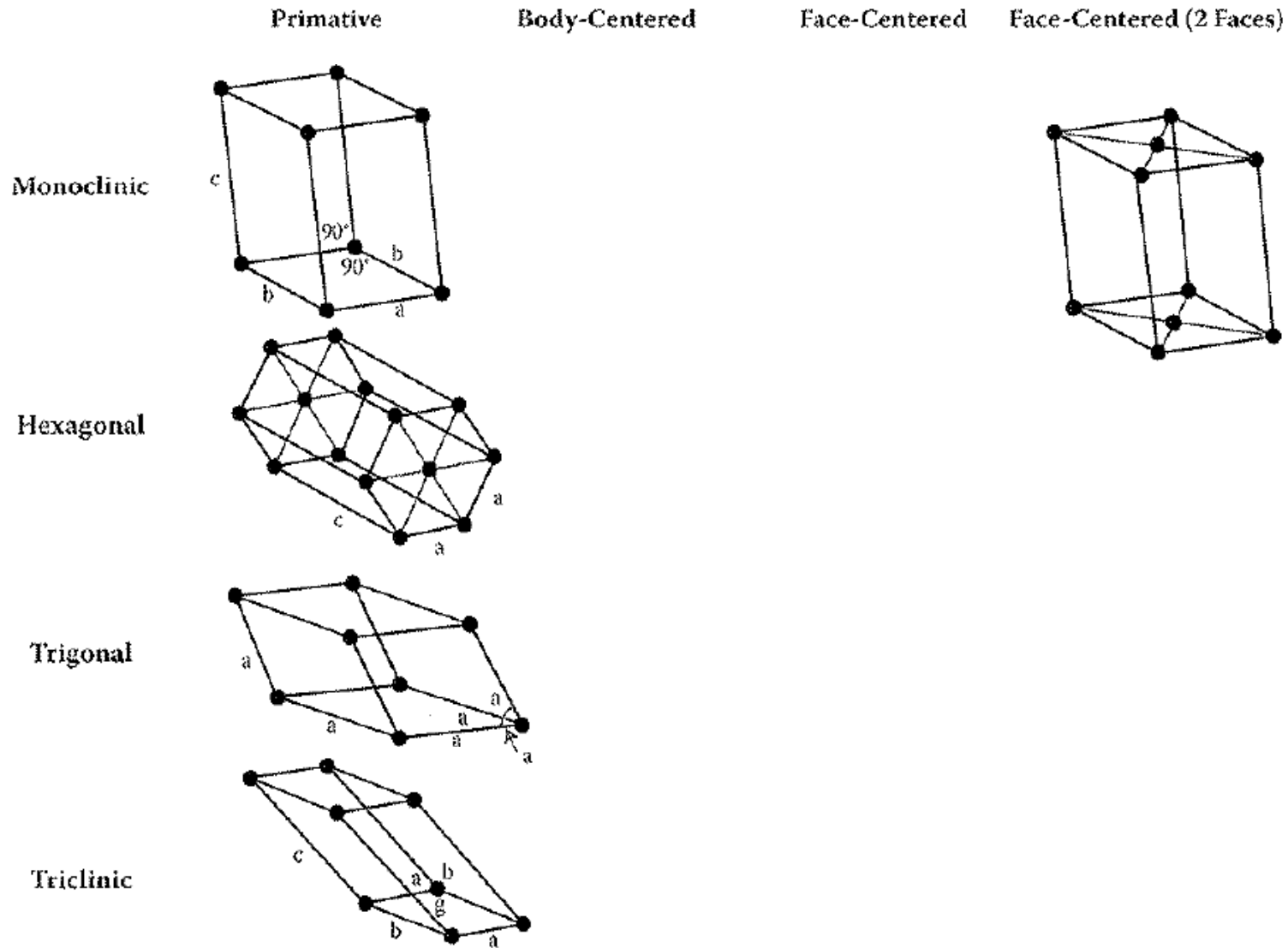
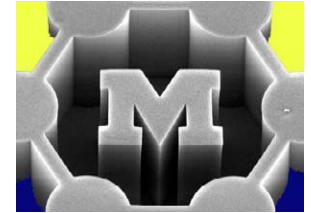
in crystal structures

more at http://en.wikipedia.org/wiki/Platonic_solid

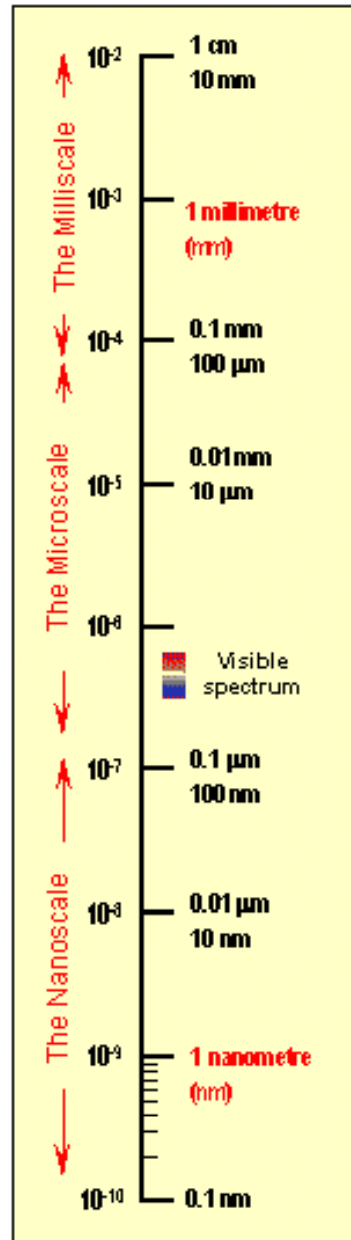
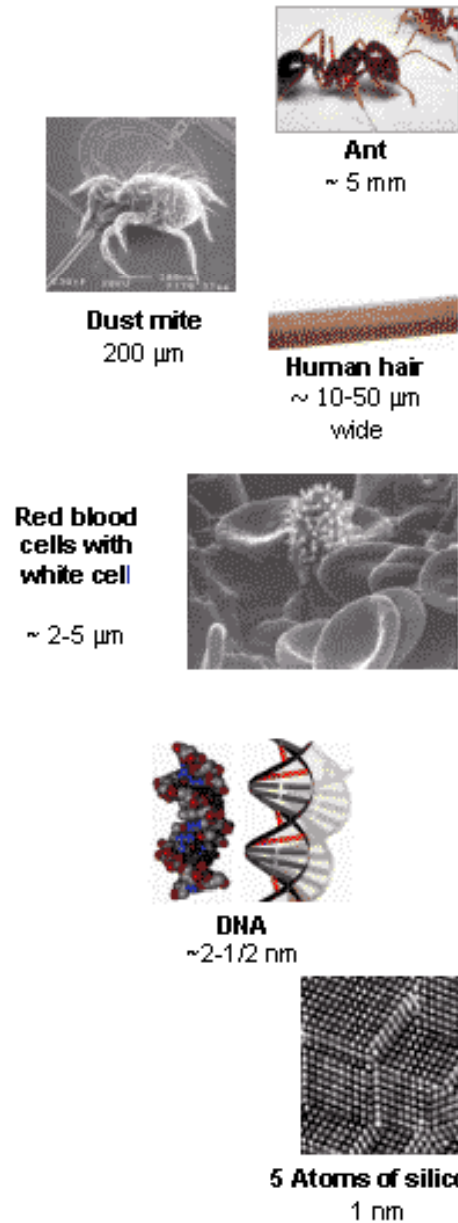
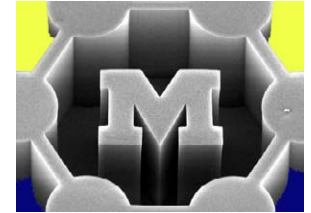
Bravais lattices*: 14 arrangements for all crystalline materials



*An infinite set of points generated by a discrete set of translation operations described by: $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$



Calibration



$$1 \text{ micrometer} = 10^{-6} \text{ m}$$

$$1 \text{ nanometer} = 10^{-9} \text{ m}$$

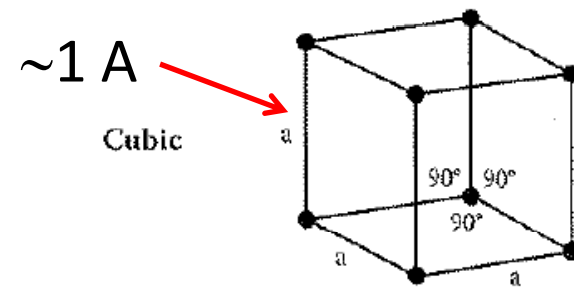
$$1 \text{ angstrom} = 10^{-10} \text{ m}$$

SO...

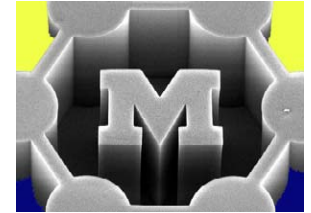
$$1 \text{ mm} = 1,000,000 \text{ μm}$$

$$1 \text{ μm} = 1000 \text{ nm}$$

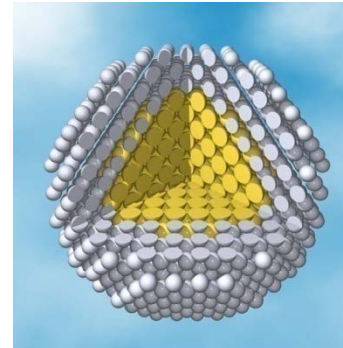
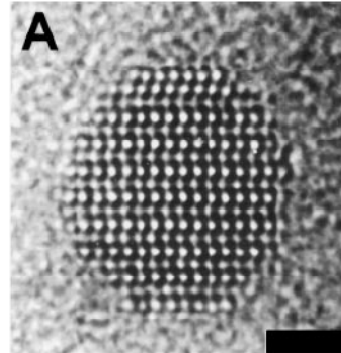
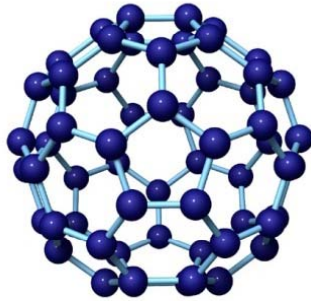
$$1 \text{ nm} = 10 \text{ A}$$



“Building blocks” – beyond molecules



0-D



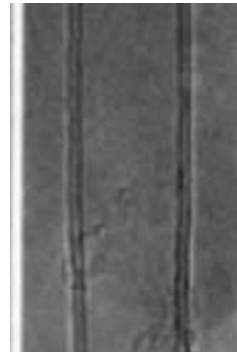
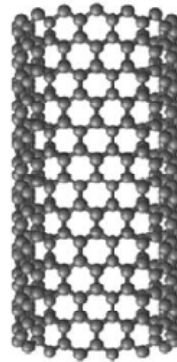
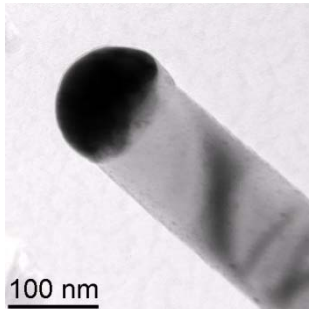
Nanoclusters

Magic #'s of atoms
≤1 nm size

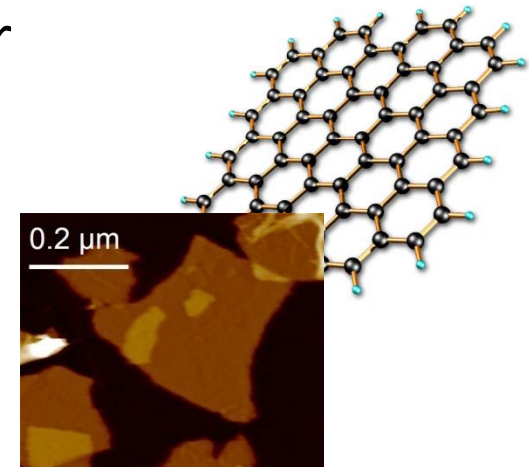
Nanoparticles

100's-1000's of atoms
~1-100 nm diameter

1-D



2-D



Nanowires

Filled

~1-100 nm dia, up to mm long and beyond!

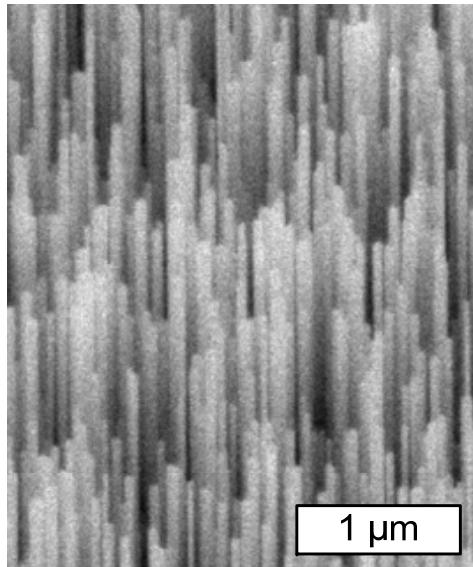
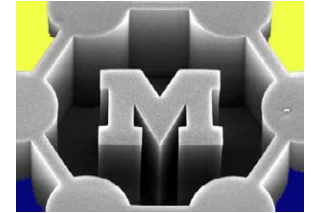
Nanotubes

Hollow

Nanosheets

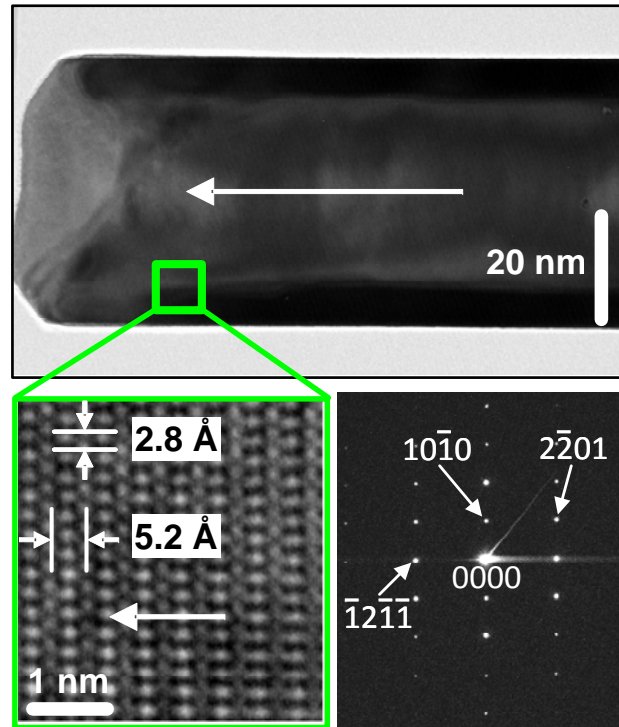
~1 atom thick

ZnO nanowires

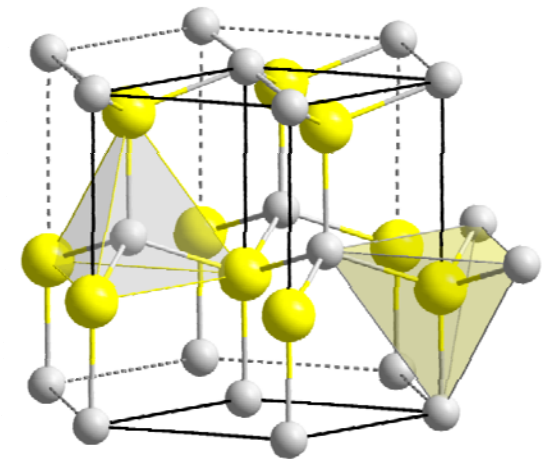


SEM image of ZnO NW array

TEM image of individual ZnO NW

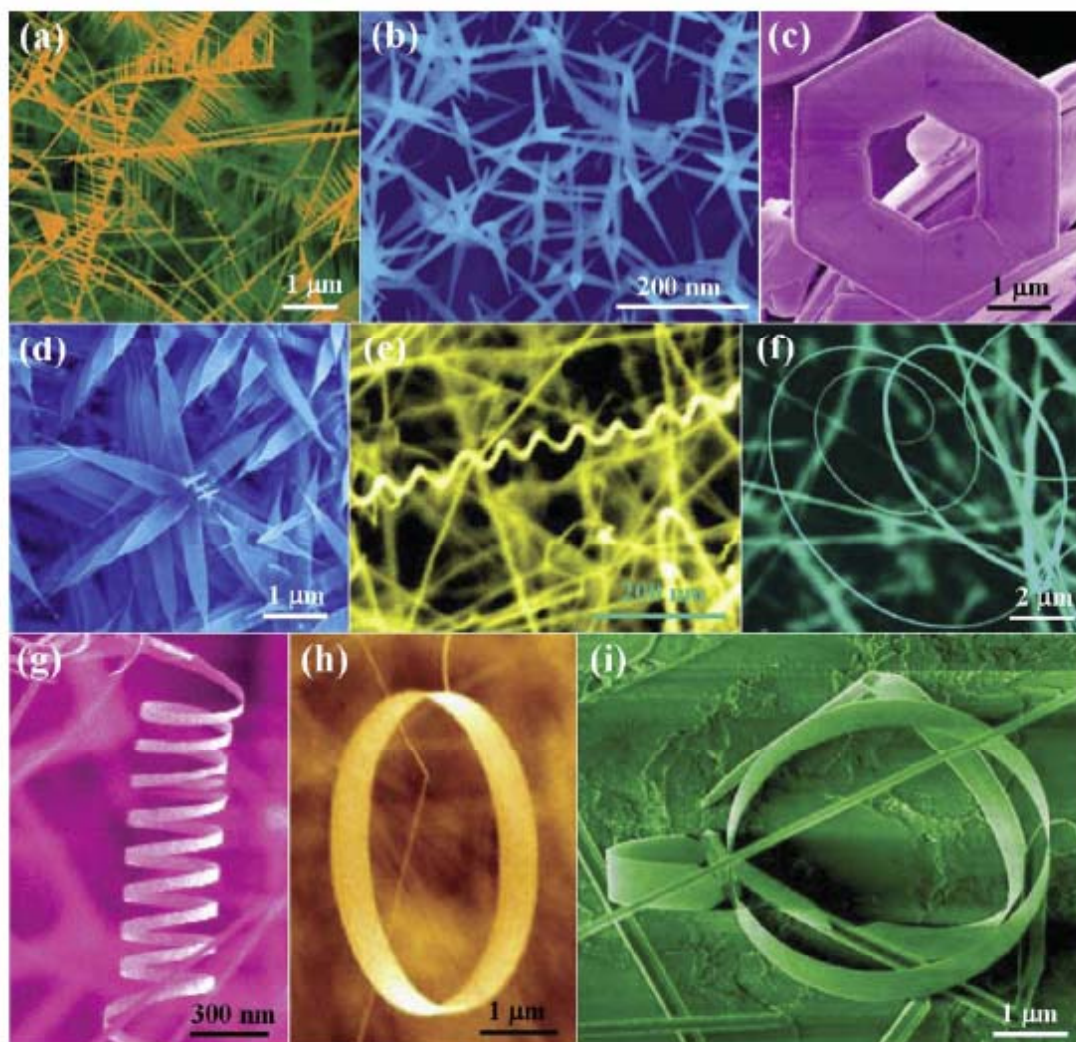
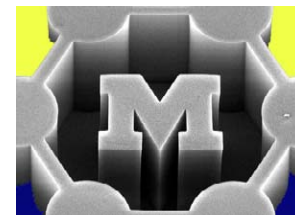


Crystal structure: hexagonal wurtzite, stacked Zn^{2+} and O^{2-}

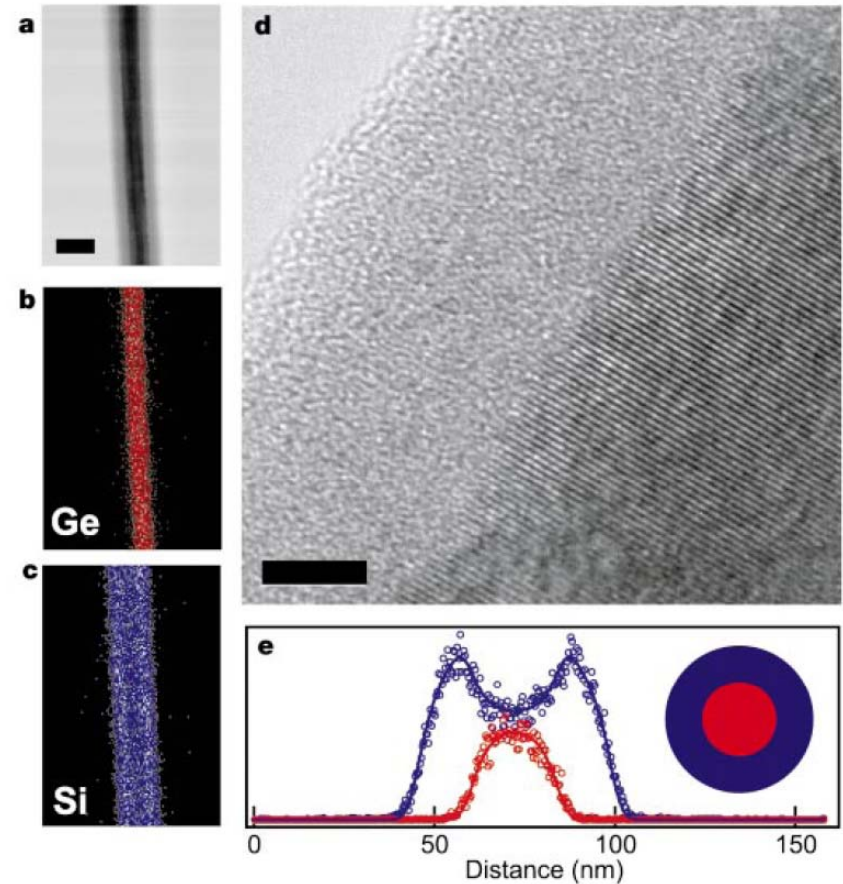
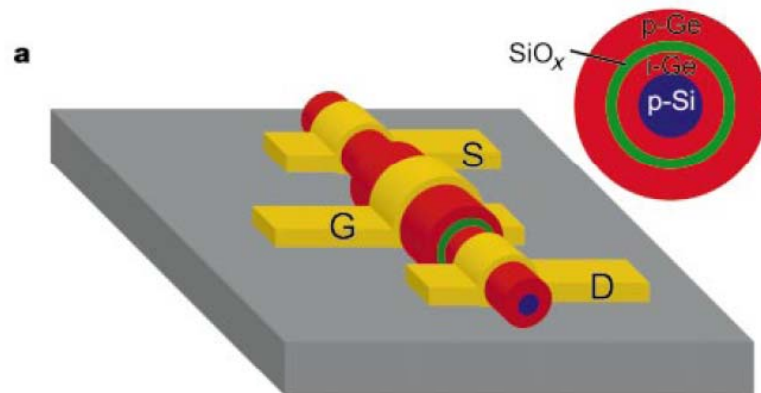
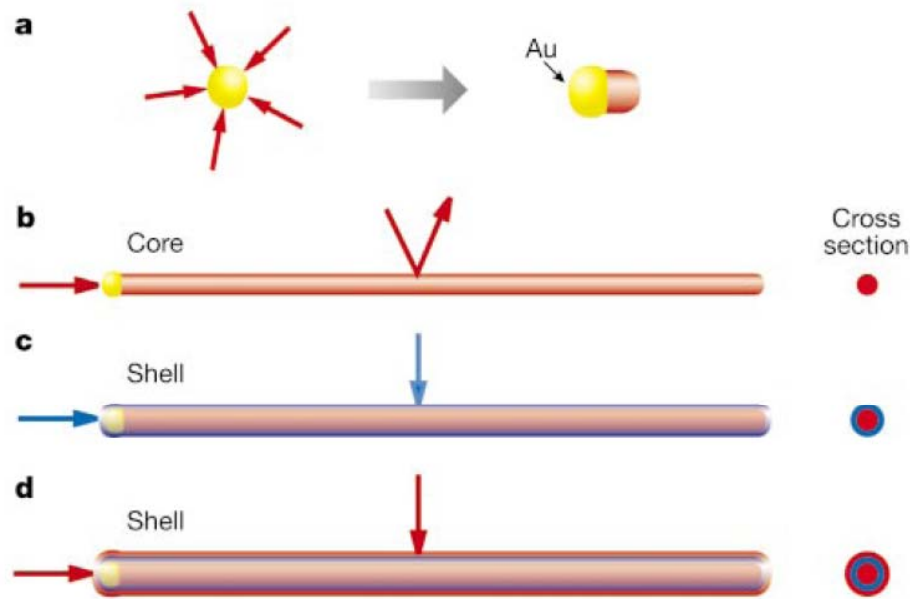
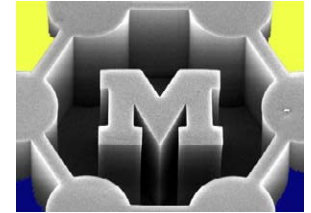


Example of diversity: ZnO

induced by epitaxy and surface polarity
there's always a polymorphic distribution

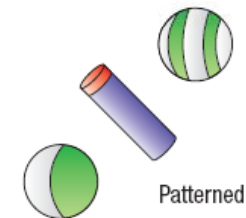
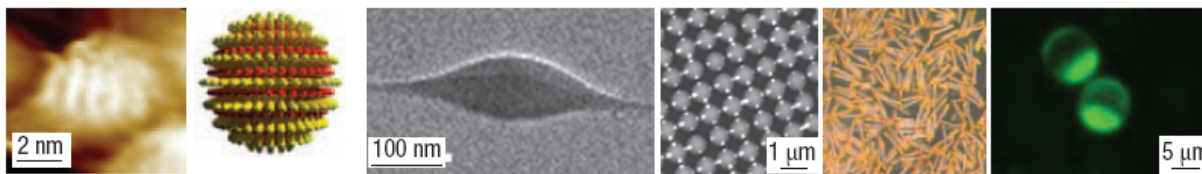
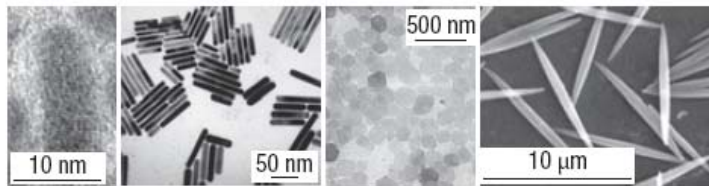
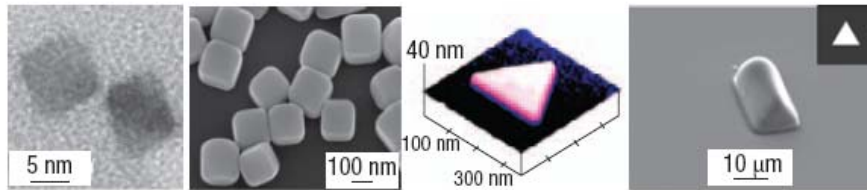
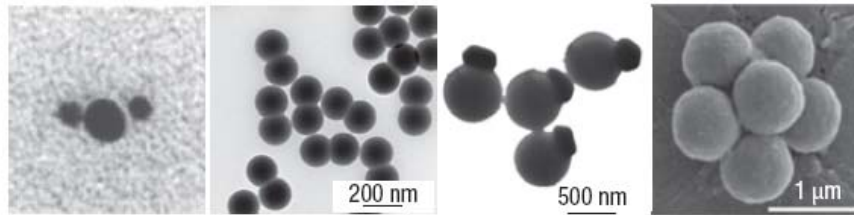
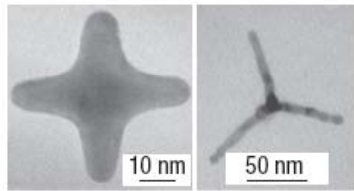
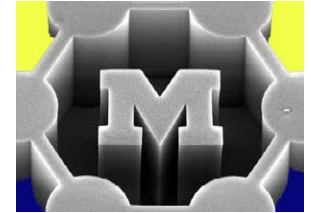


Heterostructure: core-shell nanowire



Lauhon et al, *Nature* 420, 2003.
 Qian et al, *Nano Letters* 5, 2005.


Anisotropic building blocks



Surface-to-volume ratio (S/V)



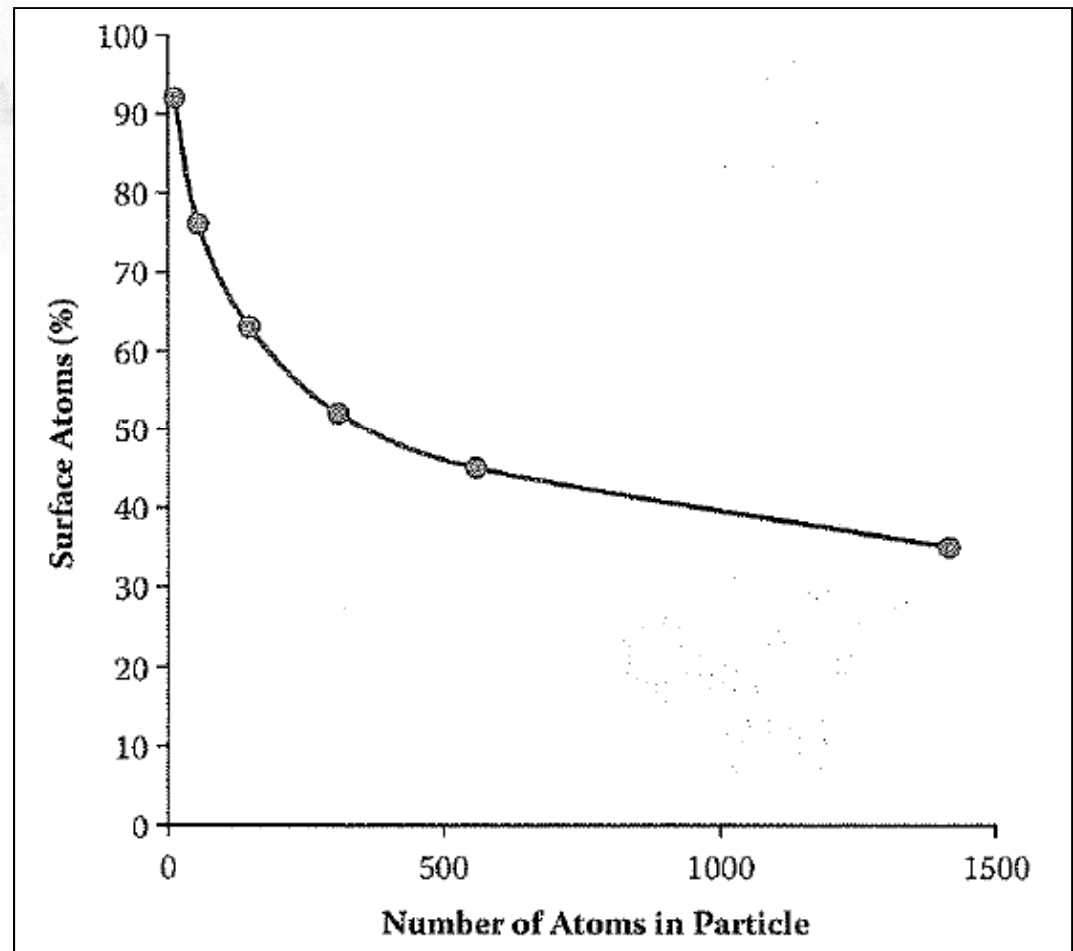
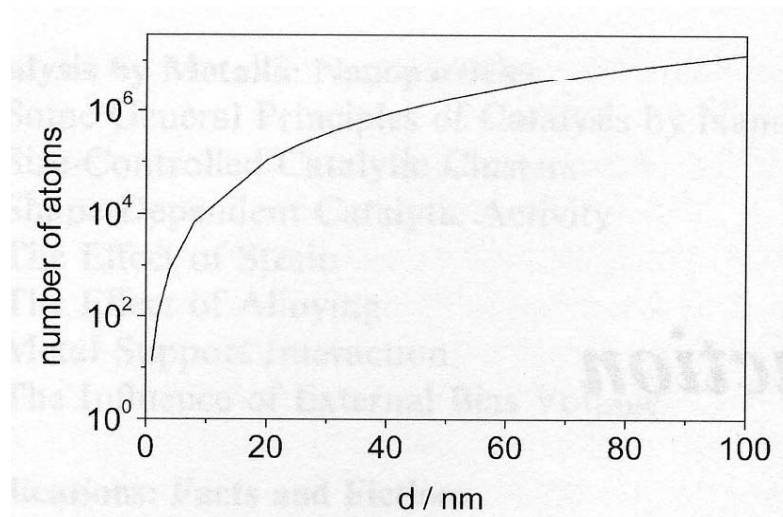
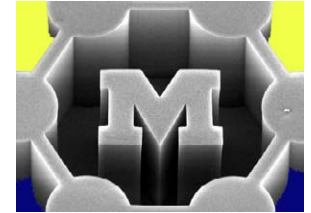
- See written notes part 1


$$\frac{SA}{V} = \frac{4\pi R^2}{\frac{4}{3}\pi R^3} = \frac{3}{R} = \frac{6}{D}$$

as $D \downarrow$ ($R \downarrow$) $\Rightarrow \frac{SA}{V} \uparrow \uparrow !$

- Q: What is different about a surface atom?

Lots of surface atoms!



Roduner, Nanoscopic Materials.

Rogers, Pennathur, Adams, Nanotechnology: Understanding Small Systems.

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Charge density oscillations at a surface

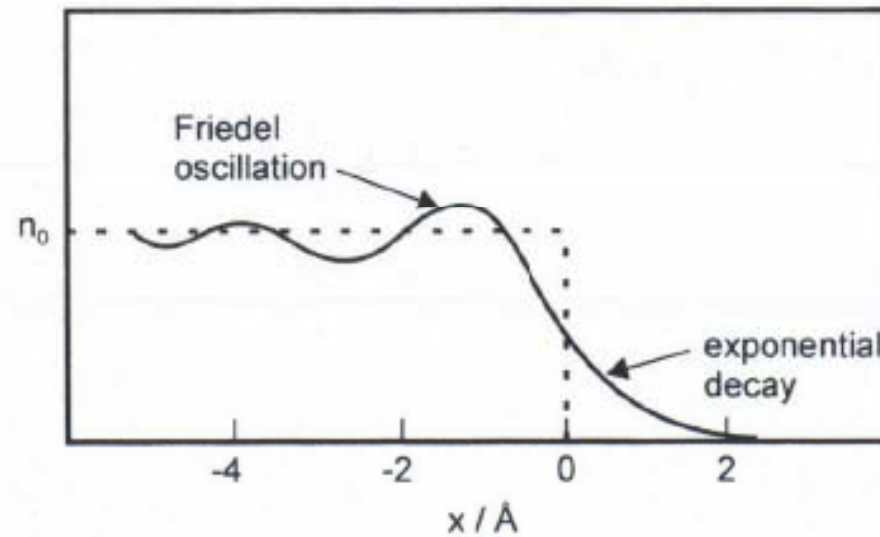
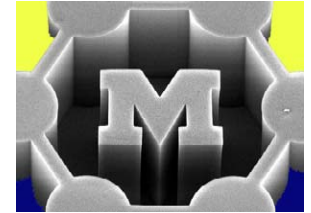


Figure 1 *Schematic drawing of the charge density distribution (Friedel oscillations) across the surface of a spin-polarised electron gas representing the conduction electrons of a metal*

(100) surface reconstruction of Si

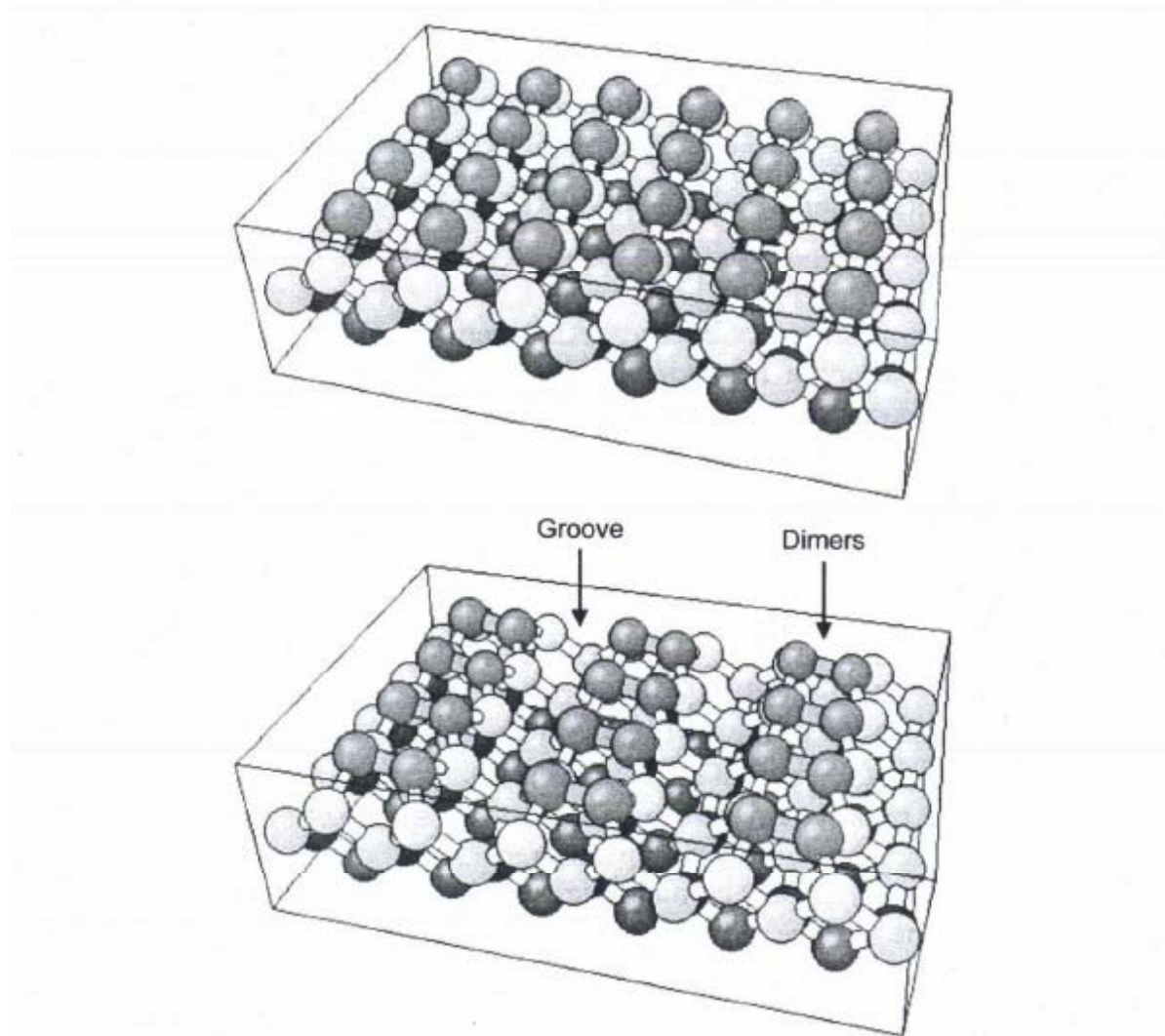
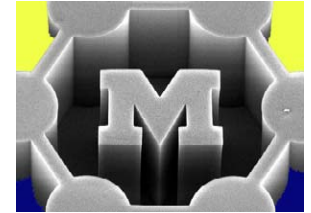
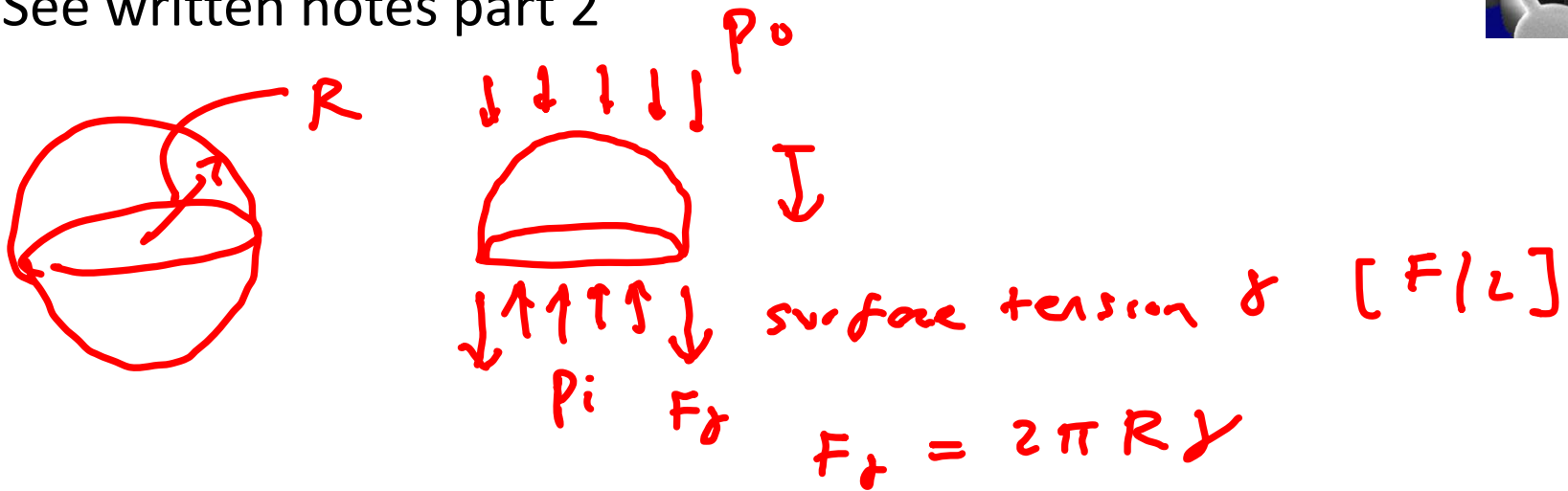


Figure 4 *Unreconstructed and reconstructed surface of a silicon (100) crystal face. Note the formation of dimers and of pronounced grooves (arrows)*

Surface pressure



- See written notes part 2



$$\sum F = 0 : 2\pi R\gamma + p_o\pi R^2 - p_i\pi R^2$$

$$-2\pi R\gamma = (p_o - p_i)\pi R^2$$

$$\Rightarrow p_o - p_i = \frac{-2\gamma}{R}$$

Lattice contraction of gold nanoparticles

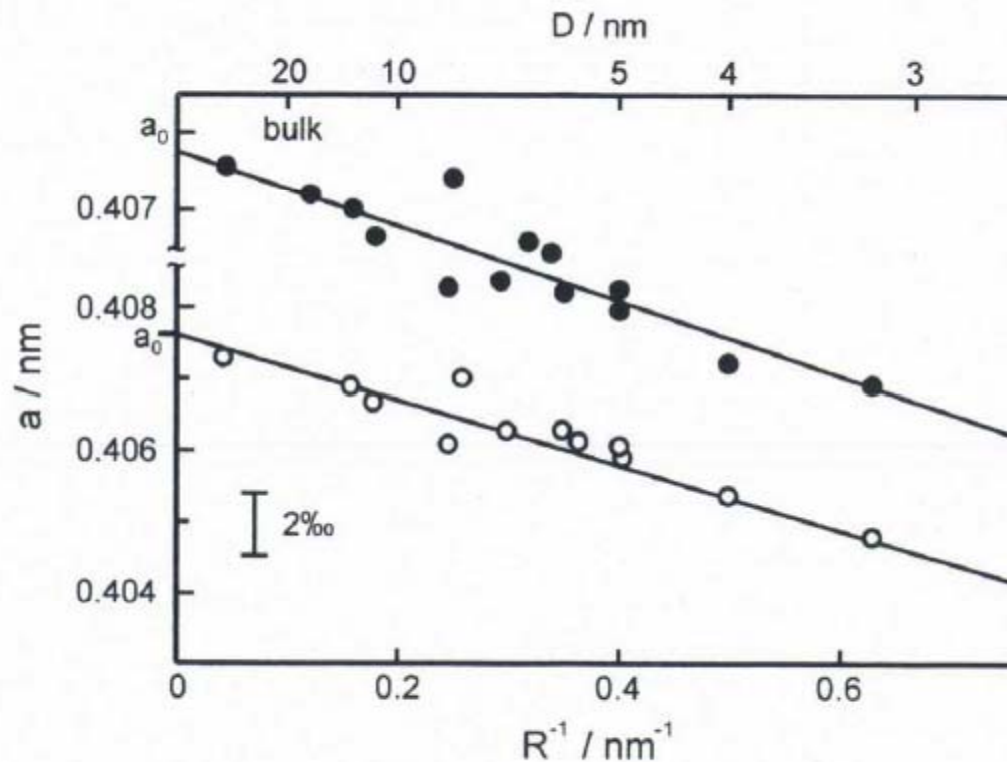
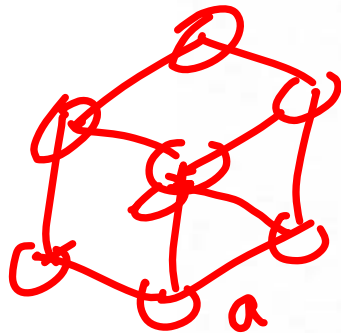
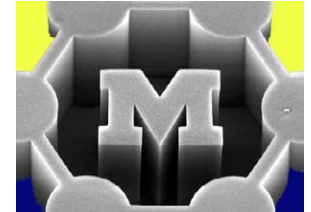


Figure 8 Average lattice parameter in gold samples deposited on a thin carbon film as a function of the reciprocal mean particle radius R (or diameter D , respectively). The parameters are derived from the (220) diffraction peak (dots) and the (422) diffraction peaks (circles). a_0 corresponds to the bulk lattice parameter (Reprinted from Ref. 17, with permission from Elsevier)

Lattice spacing changes with particle size and with distance from particle center!

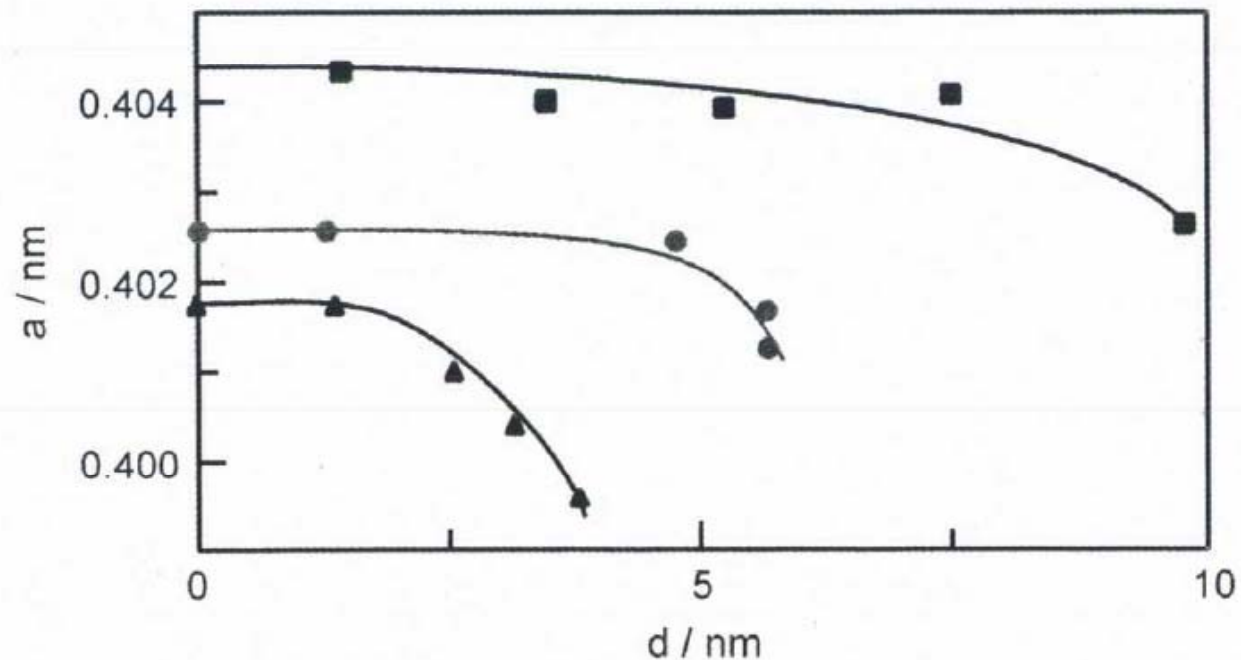
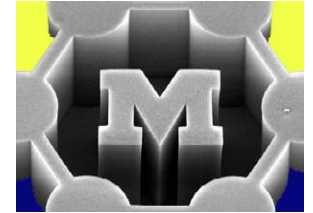
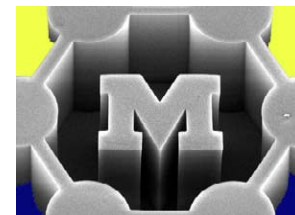


Figure 9 Variation of the lattice parameter a with the distance d from the particle centre for MgO supported Al particles with a radius of 11.4 nm (squares), 8.0 nm (circles), and 5.2 nm (triangles)
(Reprinted from Ref. 20, with permission from Elsevier)

Clusters

- Clusters are more frequently found with sizes (numbers of atoms) that represent geometrically closed shells



THE SCIENCES · March/April 1991



Richard E. Smalley, Growth of the Fullerene C₆₀, 1991

GREAT BALLS OF CARBON

The Story of Buckminsterfullerene

by RICHARD E. SMALLEY

HOW IS A FLAWLESS DIAMOND, hard and sparkling, like an ordinary pencil lead, soft and dull? A few weeks of beginning chemistry answers the riddle. Both diamond and pencil lead are made of pure carbon. In diamond the carbon atoms form a sturdy, three-dimensional lattice in which each atom is rigidly fixed at the center of a tetrahedron by bonds to four of its neighbors at the tetrahedral vertices. In pencil lead, or graphite, the carbon atoms cling together in flat sheets of contiguous hexagons that resemble the structure of chicken wire. Carbon, one of the commonest substances on earth, is also one of the best-understood. For in spite of the almost unfathomable complexity of the organic compounds it forms in living systems, carbon in its pure form has been studied for thousands of years. Until recently all the evidence suggested it forms only two basic structures, diamond and graphite.

Thus to the modern chemist a continuing study of pure carbon would seem to offer little hope for excitement. That, at least, was how it seemed in 1985, when Harold W. Kroto, a chemist from the University of Sussex in

hotter than the surfaces of most stars and certainly hot enough to vaporize any known material.

Kroto knew the laser pulses could help re-create the torrid conditions in carbon-rich red giants, and he sensed that some great and exciting science was there to be uncovered. As it turned out, what was there was more bizarre and important than any of us imagined. For we would find not only Kroto's long carbon snakes but also a previously unknown molecule of pure carbon, made of atoms bound to one another in a closed spherical network, reminiscent of the geodesic domes championed by the eccentric architect and inventor R. Buckminster Fuller.

Further research, particularly in the past year, has confirmed our initial suspicions about the domelike carbon molecules, now known as fullerenes. Here, in fact, is a third basic form of pure carbon, the first new form to be discovered since the dawn of chemistry several hundred years ago. The molecule is remarkably stable and impervious to radiation and chemical erosion, properties that could lead to many important commercial applications in

“Magic numbers” in a plane

- Atom counting

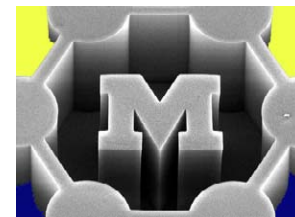
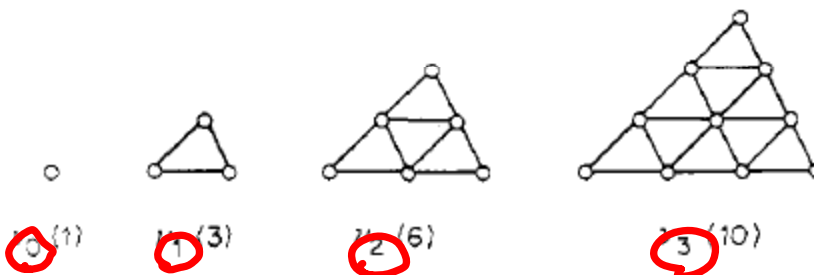


Chart I. Triangles of Frequency 0, 1, 2, and 3^a



^a The triangles need not have equal sides. The numbers of points (the triangular numbers t_0, t_1, t_2, t_3) are given in parentheses. A triangle of frequency n , or a ν_n triangle, contains $n + 1$ points on each edge.

# atoms	1	3	6	10
frequency (n)	0	1	2	3

Magic numbers: counting triangles



- See written notes part 3

2D, polygon

$F = \# \text{ triangles}$

$p = \# \text{ sides}$

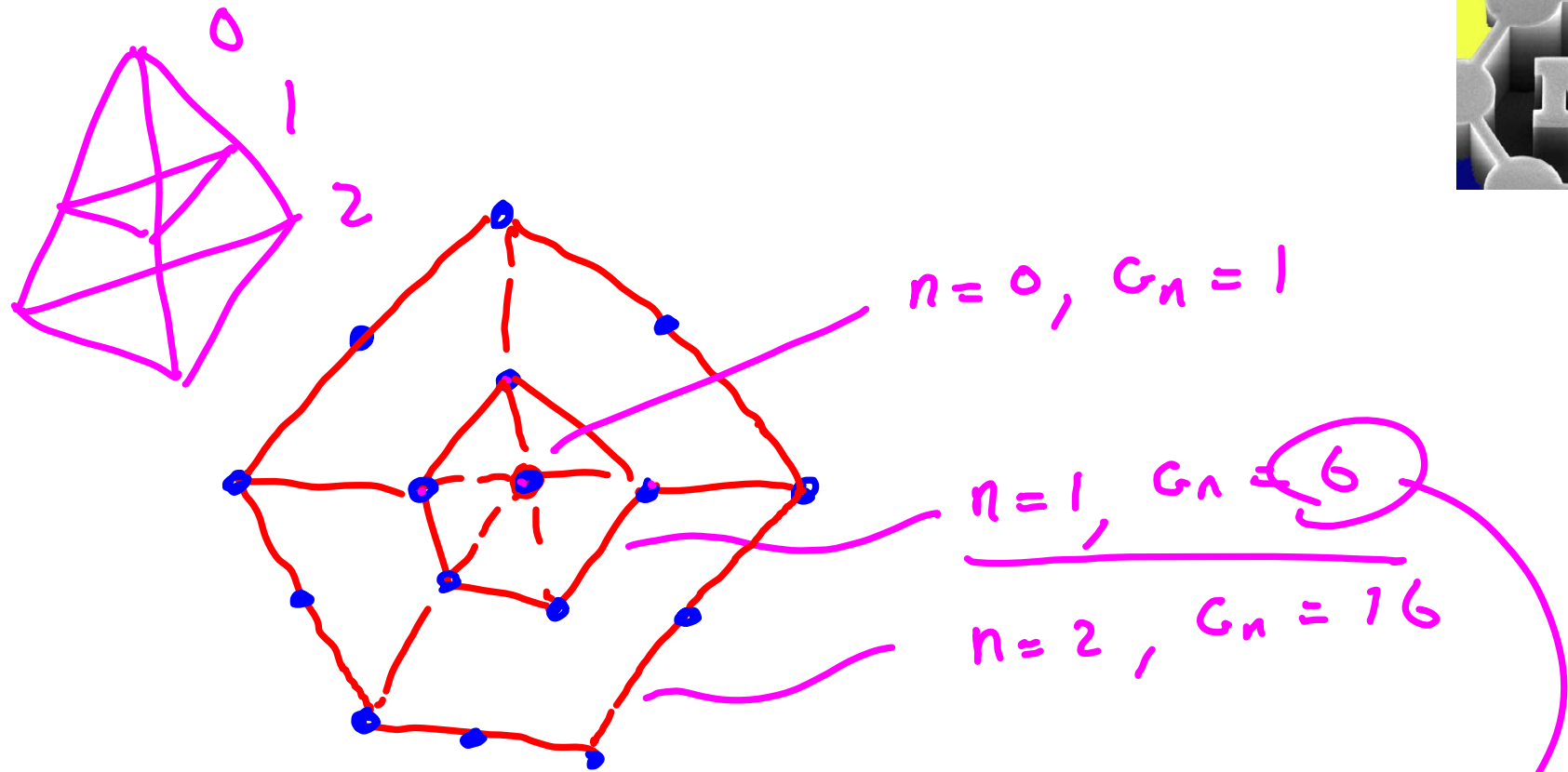
$n = \text{frequency}$

total # stars

$$G_n = \frac{1}{2} F n^2 + \frac{1}{2} p n + 1$$

surface $S_n = p n$

$$G_n - S_n : \text{ "interior stars" } = \frac{1}{2} F n^2 - \frac{1}{2} p n + 1$$



$$G_n = \frac{1}{2} F n^2 + \frac{1}{2} p n + 1$$
$$\frac{1}{2} 5 \cdot 1 + \frac{1}{2} \cdot 5 \cdot 1 + 1 = 6$$

Magic numbers: 2D

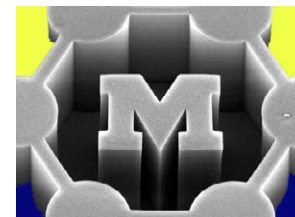


Chart VII. Centered Pentagons of Frequency 0, 1, 2, and 3 and the Centered Pentagonal Numbers ($p = F = 5$)

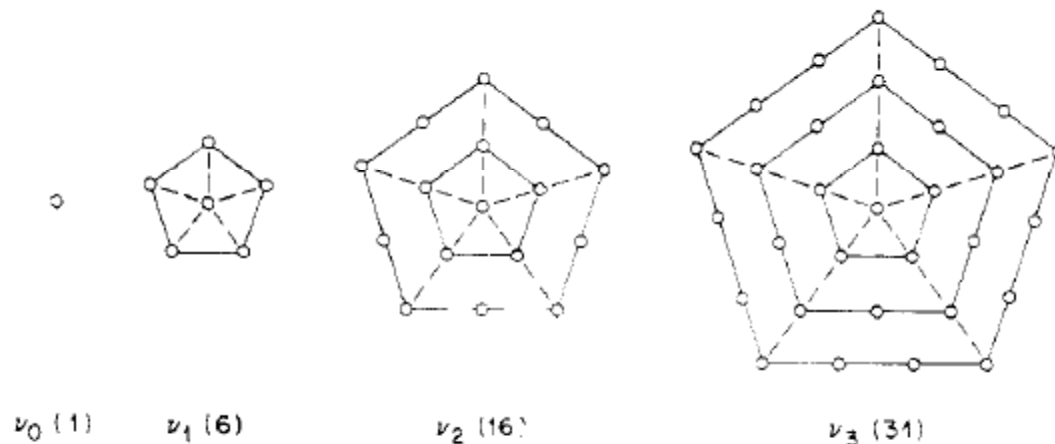
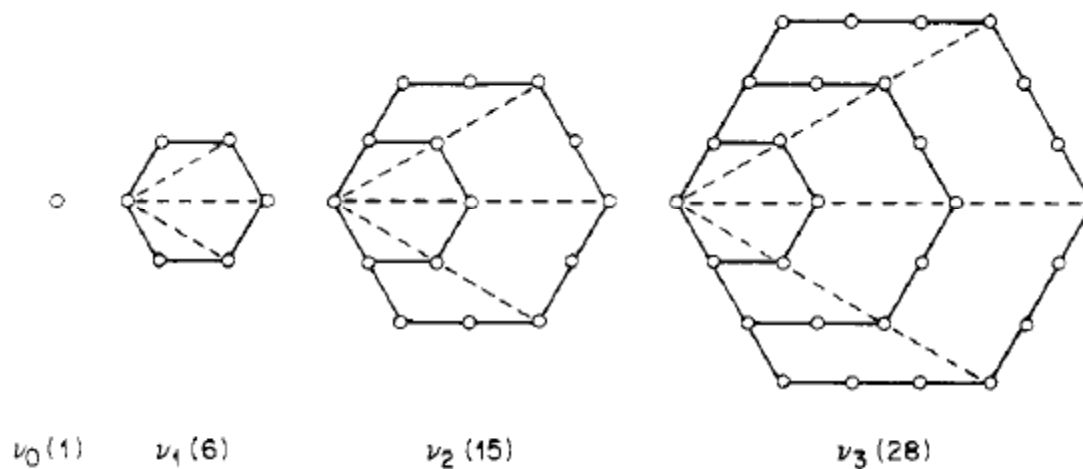


Chart VIII. Regular Hexagons of Frequency 0, 1, 2, and 3 and the Classical Hexagonal Numbers ($p = 6, F = 4$)



Magic numbers: 3D

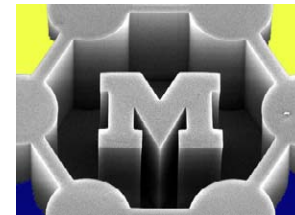
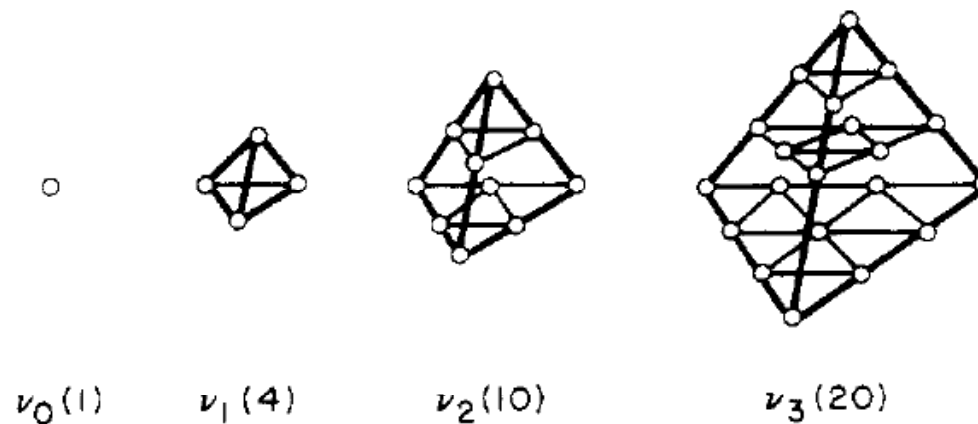
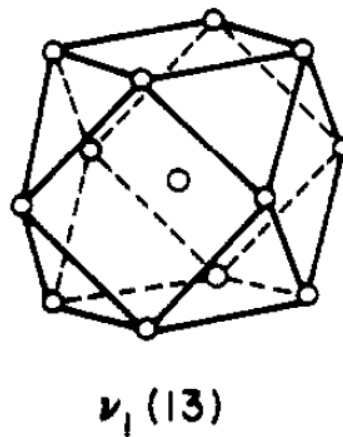


Chart XIII. Tetrahedra of Frequency 0, 1, 2, and 3^a

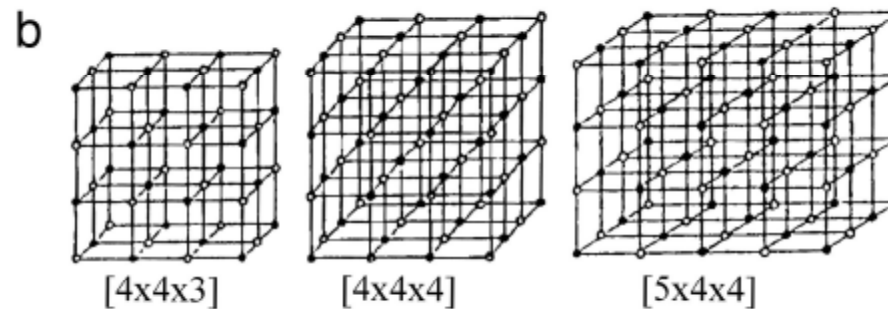
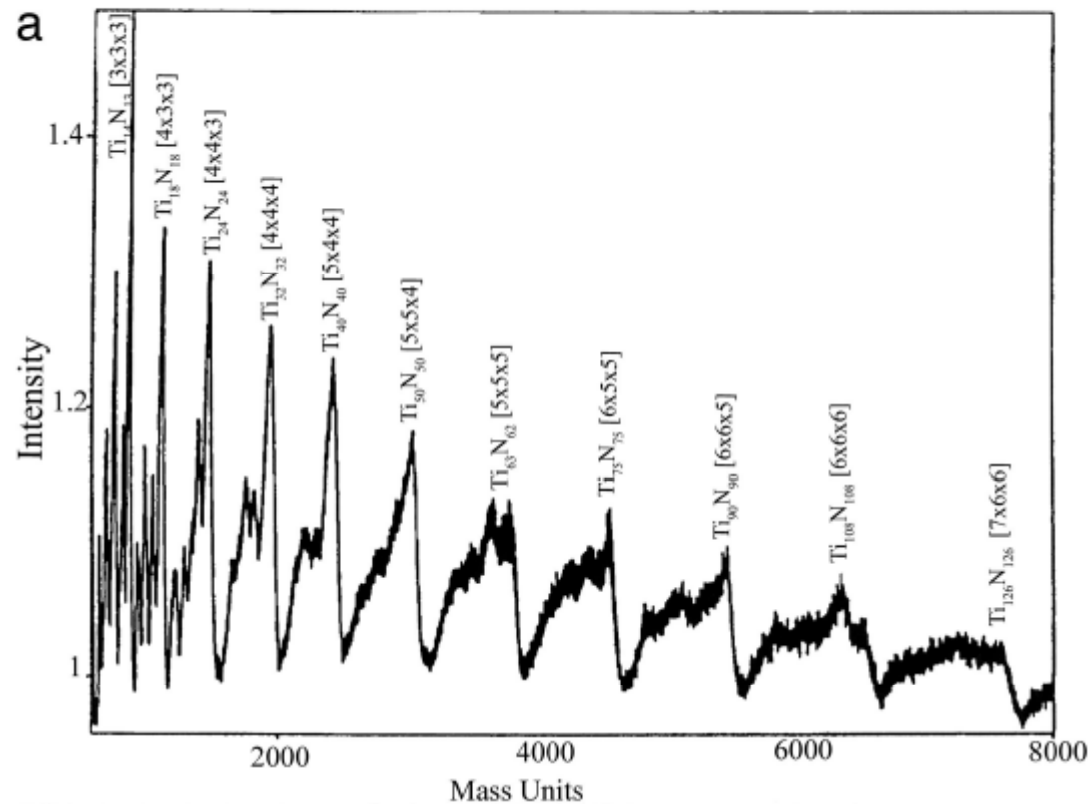
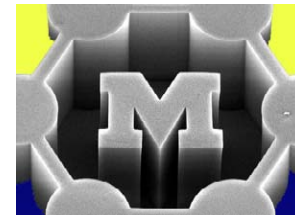


^a The numbers in parentheses are the tetrahedral numbers σ_n (see eq 41).

Chart XX. Cuboctahedron of Frequency 1



Magic number clusters of $[\text{TiN}]_n$



Making and measuring clusters

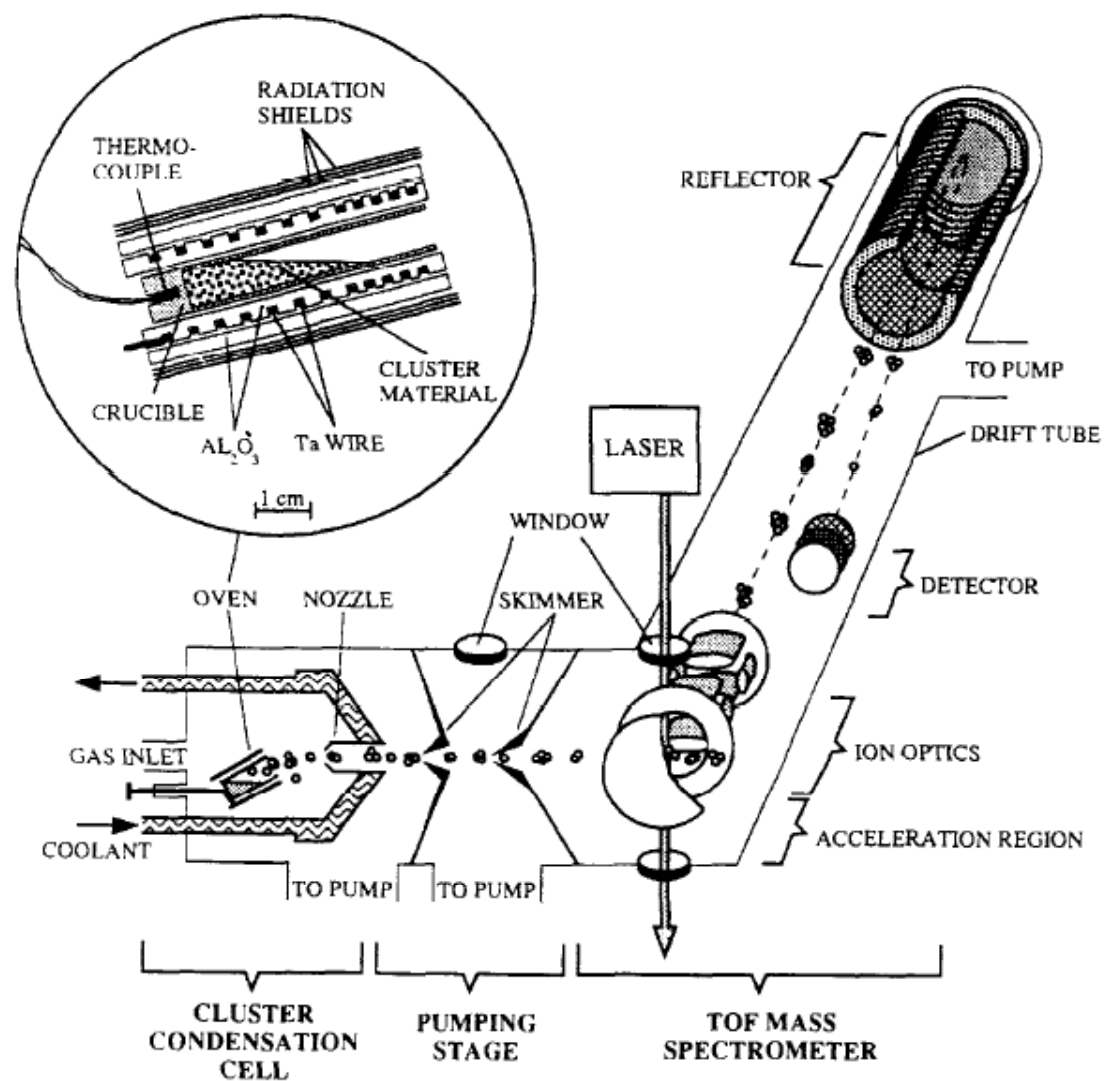
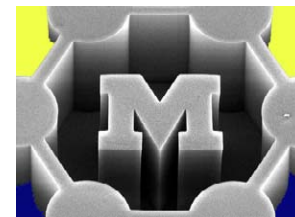
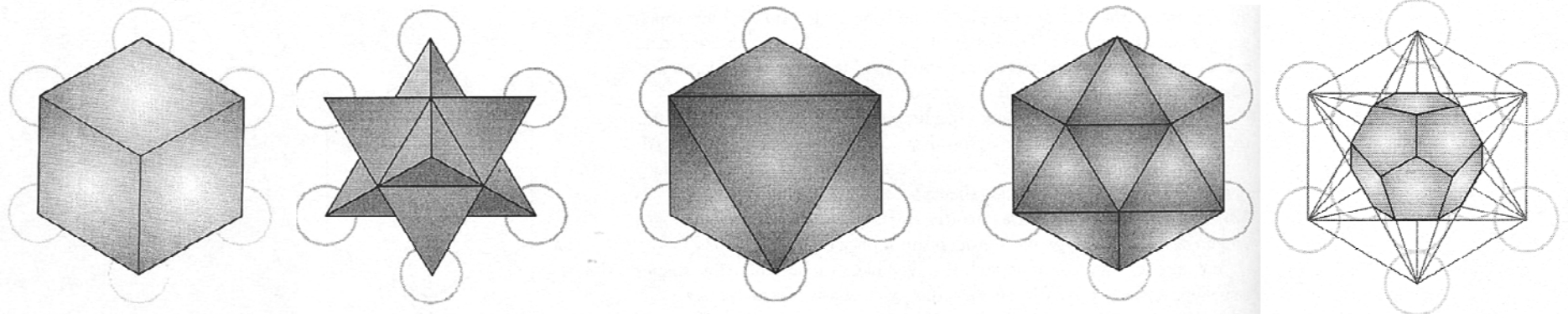
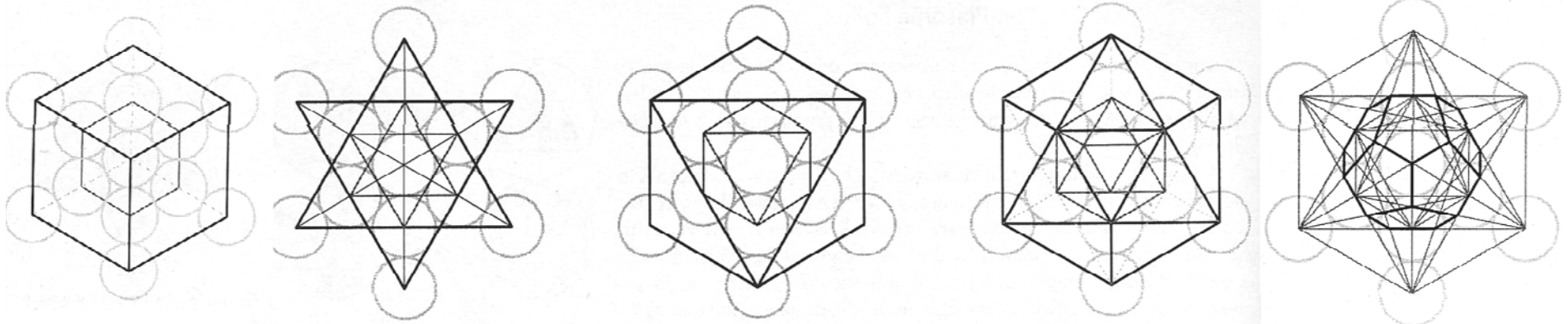
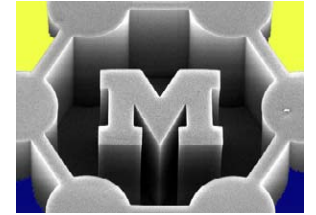


Fig. 17. Apparatus for the production, photoionization and time-of-flight mass analysis of clusters.

The platonic solids



Cube

Star
Tetrahedron

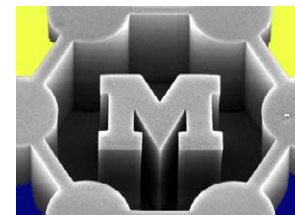
Octahedron

Icosahedron

Dodecahedron

more at http://en.wikipedia.org/wiki/Platonic_solid

“Choice” of cluster geometry depends on crystal structure



FCC nanoparticle (e.g., Au)

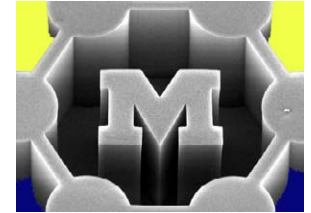
Table VI. Number of Surface Points (S_n) and the Total Number of Points (G_n) in Platonic Solids of Frequency n^a

Polyhedron	n	0	1	2	3	4	5	6	7	8	9	10
tetrahedron	S_n	1	4	10	20	34	52	74	100	130	164	202
	G_n	1	4	10	20	35	56	84	120	165	220	286
centered tet. [*] cube	G_n	1	5	15	35	69	121	195	295	425	589	791
	S_n	1	8	26	56	98	152	218	296	386	488	602
centered cube [*] octahedron	G_n	1	8	27	64	125	216	343	512	729	1000	1331
	S_n	1	6	18	38	66	102	146	198	258	326	402
centered icosahedron	G_n	1	6	19	44	85	146	231	344	489	670	891
	S_n	1	12	42	92	162	252	362	492	642	812	1002
centered dodecahedron	G_n	1	13	55	147	309	561	923	1415	2057	2869	3871
	S_n	1	32	122	272	482	752	1082	1472	1922	2432	3002
G_n	1	33	155	427	909	1661	2743	4215	6137	8569	11571	

Table VII. Number of Surface Points (S_n) and the Total Number of Points (G_n) for Various Archimedean and Other Figures

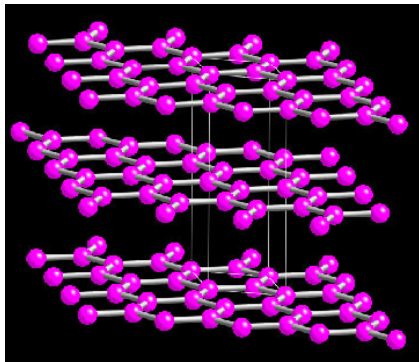
Polyhedron	n	0	1	2	3	4	5	6	7	8	9	10
truncated tetrahedron	S_n	1	16	58	128	226	352	506	688	898	1136	1402
	G_n	1	16	68	180	375	676	1106	1688	2445	3400	4576
cubocta- -hedron ^a	S_n	1	12	42	92	162	252	362	492	642	812	1002
	G_n	1	13	55	147	309	561	923	1415	2057	2869	3871
truncated octahedron	S_n	1	32	122	272	482	752	1082	1472	1922	2432	3002
	G_n	1	38	201	586	1289	2406	4033	6266	9201	12934	17561
truncated ν_3 cube	S_n	1	48	186	416	738	1152	1658	2256	2946	3728	4602
	G_n	1	56	311	920	2037	3816	6411	9976	14665	20632	28031
triangular prism	S_n	1	6	18	38	66	102	146	198	258	326	402
	G_n	1	6	18	40	75	126	196	288	405	550	726
hexagonal prism	S_n	1	14	50	110	194	302	434	590	770	974	1202
	G_n	1	14	57	148	305	546	889	1352	1953	2710	3641
rhombic dodecahedron	S_n	1	14	50	110	194	302	434	590	770	974	1202
	G_n	1	15	65	175	369	671	1105	1695	2465	3439	4641
square pyramid ^b	S_n	1	5	14	29	50	77	110	149	194	245	302
	G_n	1	5	14	30	55	91	140	204	285	385	506
tricapped prism	S_n	1	9	30	65	114	177	254	345	450	569	702
	G_n	1	9	33	82	165	291	469	708	1017	1405	1881

The allotropes* of carbon



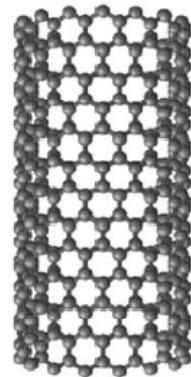
CNTs

Graphite
 sp^2



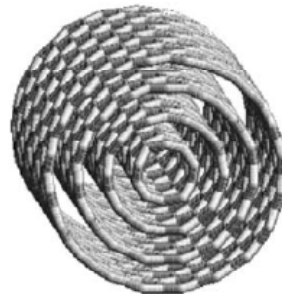
Single-wall CNT (SWNT)

D = 0.4-3 nm



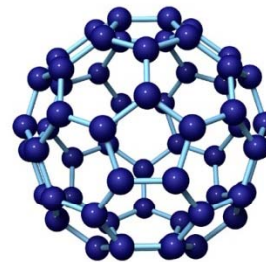
Multi-wall CNT (MWNT)

D = 3-100 nm

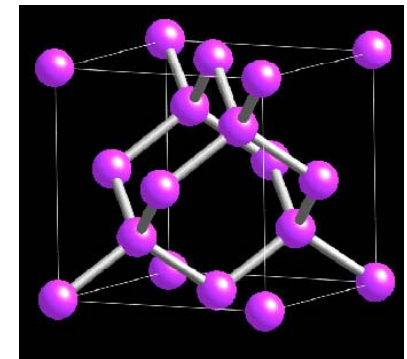


Fullerene

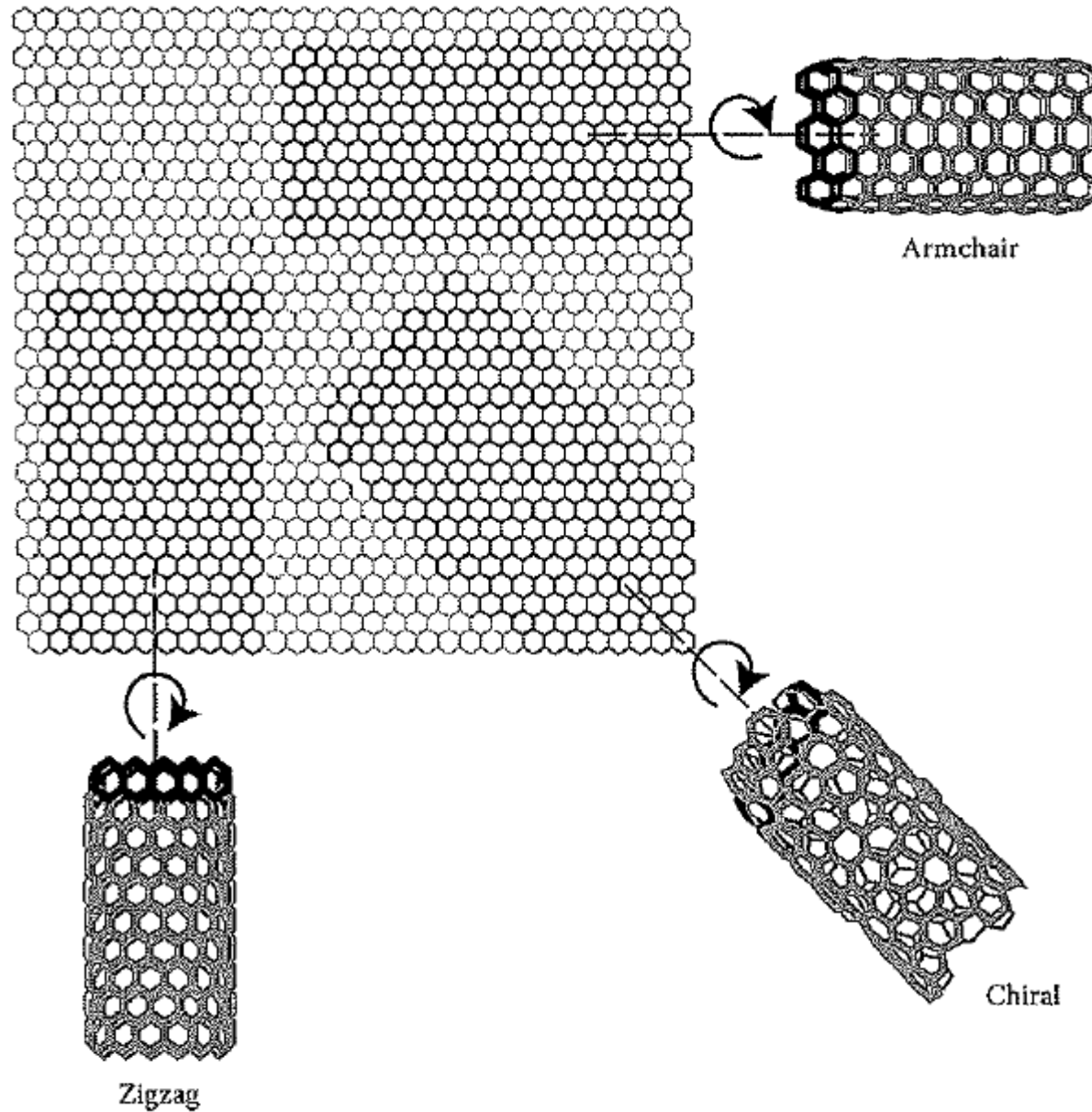
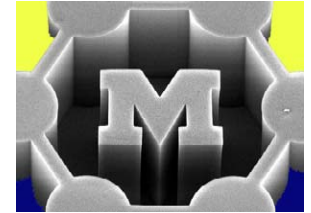
D = 0.4-3 nm



Diamond
 sp^3



Carbon nanotubes (CNTs)



CNTs: unit vectors and chiral vector

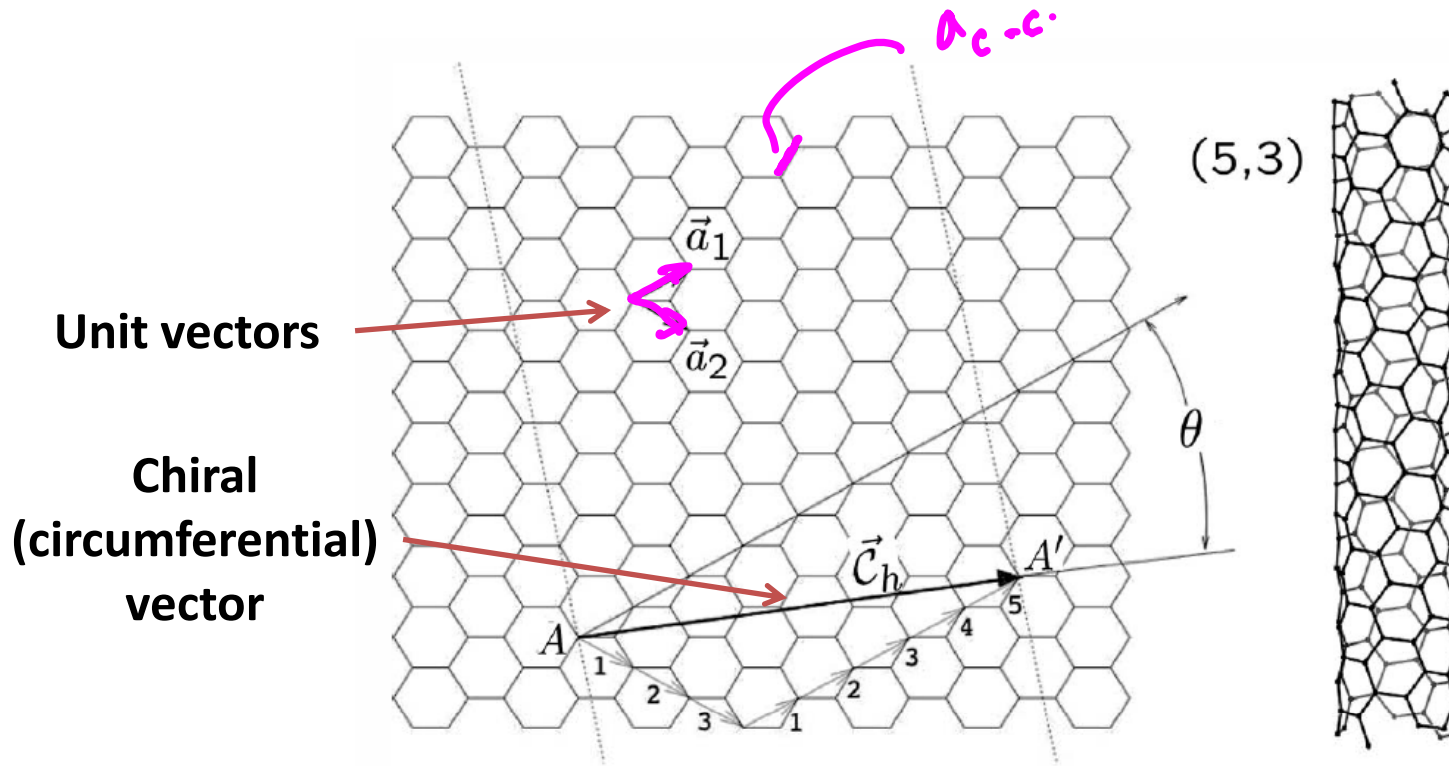
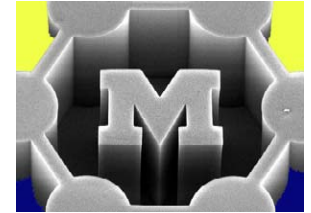


FIG. 2. Graphene honeycomb network with lattice vectors \mathbf{a}_1 and \mathbf{a}_2 . The chiral vector $\mathbf{C}_h = 5\mathbf{a}_1 + 3\mathbf{a}_2$ represents a possible wrapping of the two-dimensional graphene sheet into a tubular form. The direction perpendicular to \mathbf{C}_h is the tube axis. The chiral angle θ is defined by the \mathbf{C}_h vector and the \mathbf{a}_1 zigzag direction of the graphene lattice. In the present example, a (5,3) nanotube is under construction and the resulting tube is illustrated on the right.

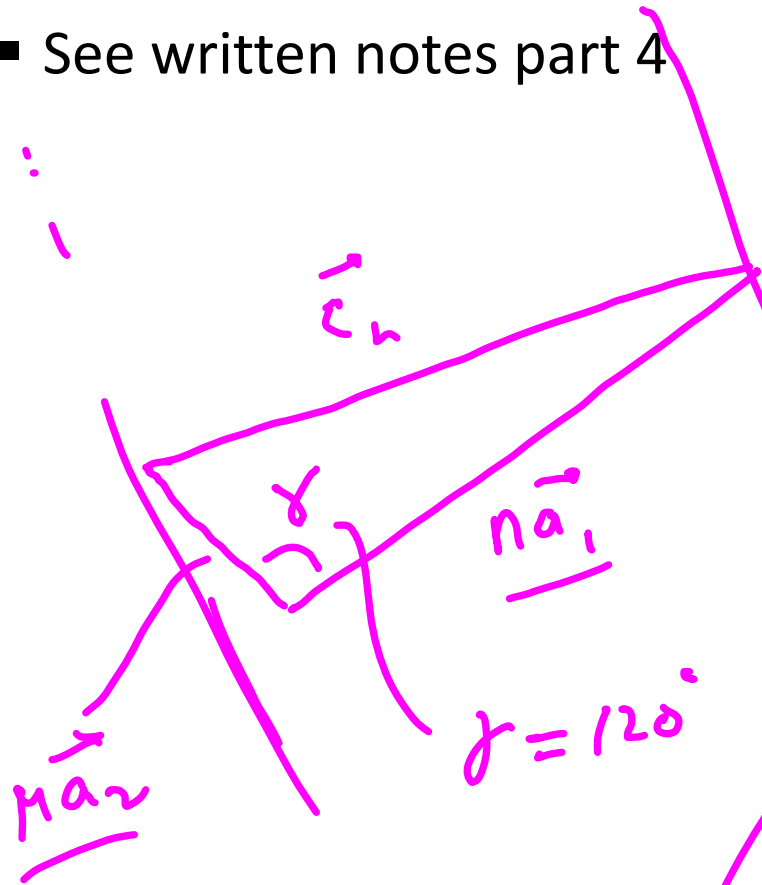
$$\begin{aligned}
 \vec{C}_h &= \\
 n\vec{a}_1 + \\
 m\vec{a}_2 \\
 |\vec{a}_1| &= \\
 |\vec{a}_2| &= \\
 &= \sqrt{3} a_{c-c} \\
 &= 2.46 \text{ \AA}
 \end{aligned}$$

$$a_{c-c} = 1.44 \text{ \AA}$$

A CNT as a crystal



- See written notes part 4



law of cosines

$$|c_h|^2 = \overbrace{n^2 a^2} + |m \bar{a}_2|^2 - 2 |n \bar{a}_1| |m \bar{a}_2| \cos \gamma$$

$$\cos \gamma = -\frac{1}{2}$$

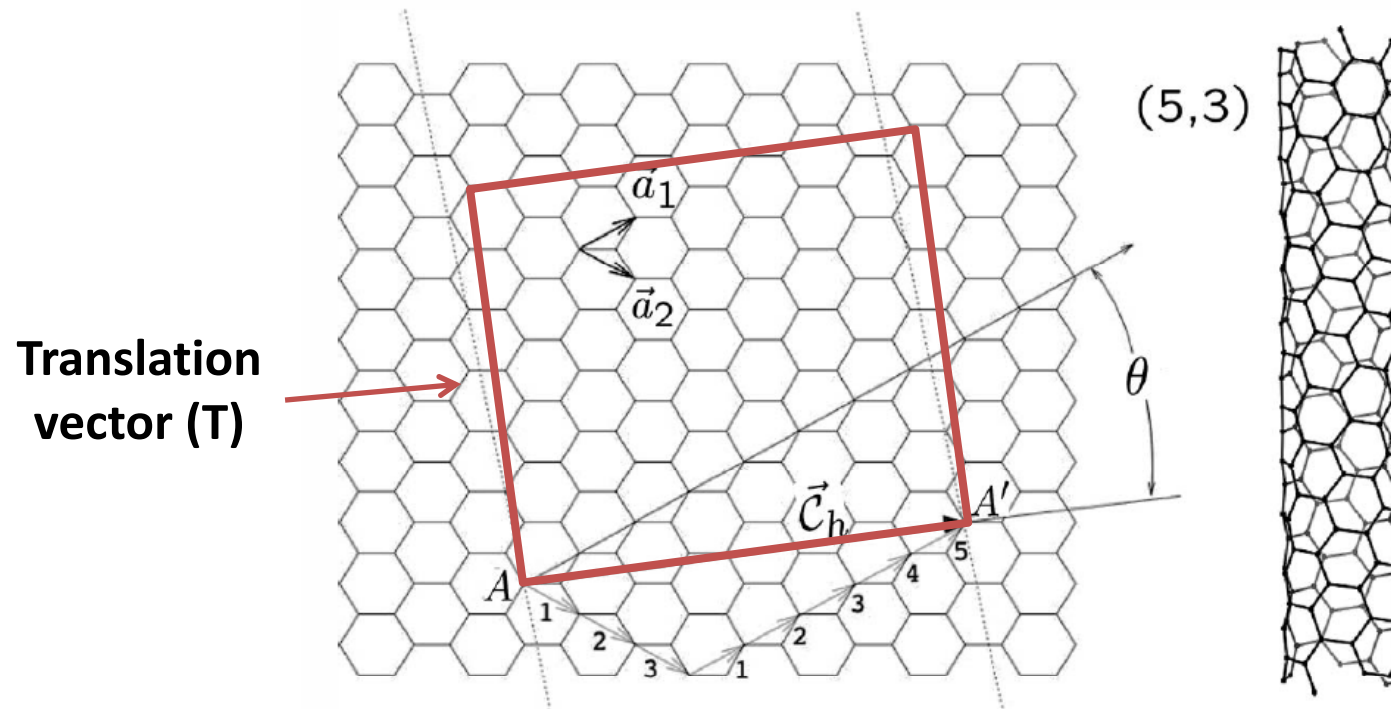
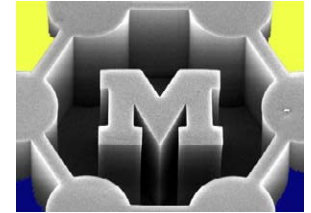
$$|\bar{a}_1| = |\bar{a}_2| = a = 2.46 \text{ \AA}$$

$$|c_h|^2 = \underline{n^2 a^2 + m^2 a^2 + 2nm a^2 \left(\frac{1}{2}\right)}$$

$$d = \frac{|c_h|}{\pi} = \frac{a}{\pi} \sqrt{n^2 + m^2 + nm}$$



CNT unit cell



Zigzag, armchair, and chiral CNTs

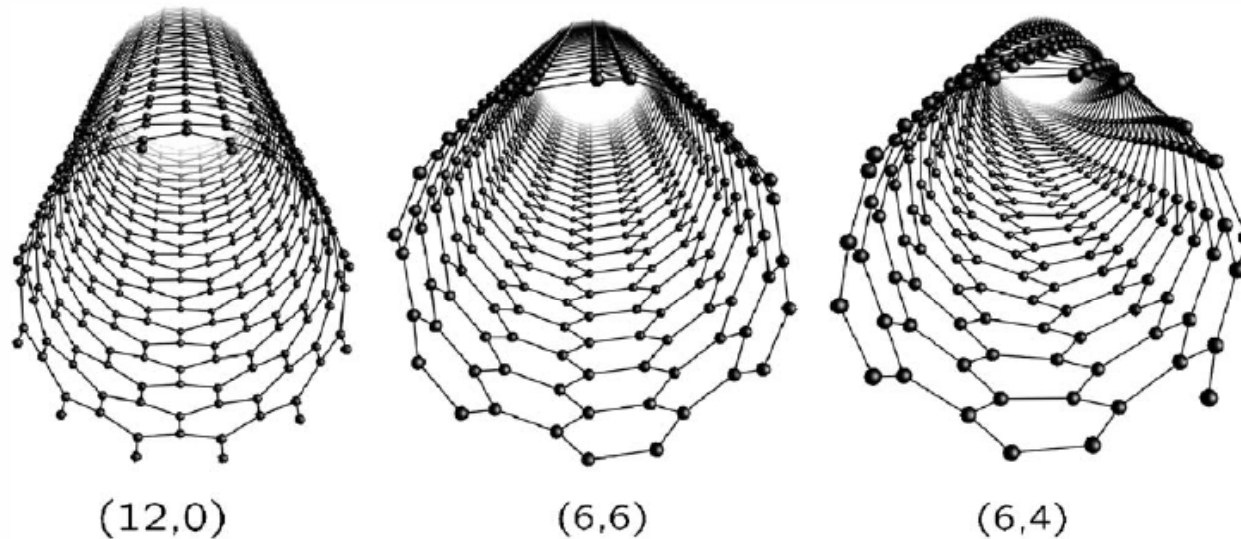
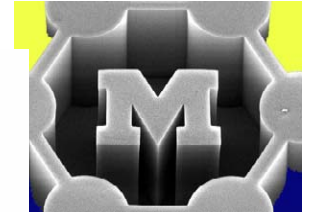




FIG. 3. Atomic structures of (12,0) zigzag, (6,6) armchair, and (6,4) chiral nanotubes.

Table 3.1: Classification of carbon nanotubes.

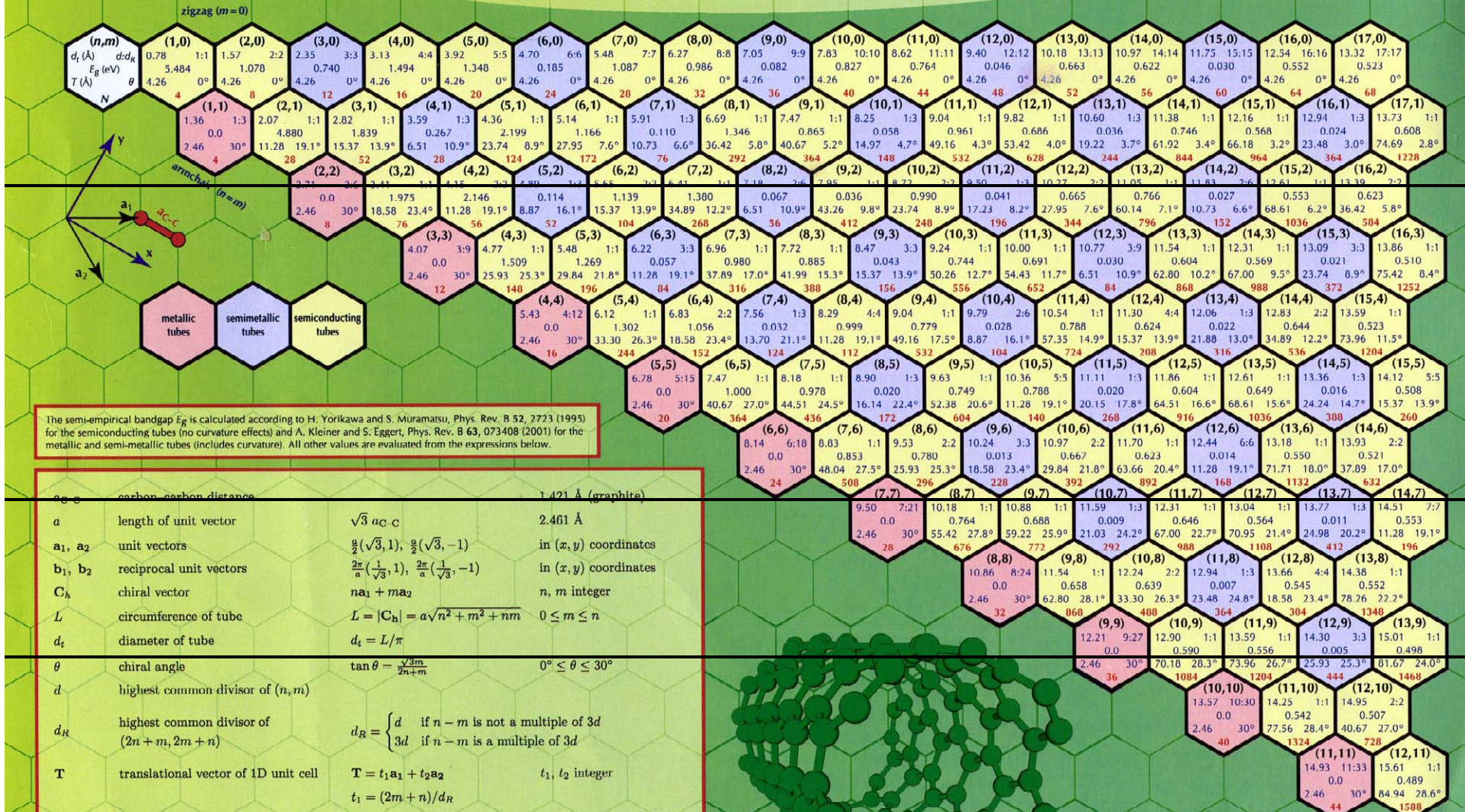
Type	$\theta^a)$	$C_h^b)$	Shape of cross section	Symmetry ^{c)}
armchair	30°	(n, n)	<i>cis</i> -type 	$D_n \otimes C_i$
zigzag	0°	$(n, 0)$	<i>trans</i> -type 	$D_n \otimes C_i$
chiral	$0^\circ < \theta < 30^\circ$	(n, m)	mixture of <i>cis</i> and <i>trans</i>	$C_d \otimes C_{N/d}$

^{a)} The chiral angle θ is defined by Eq. (3.4).

^{b)} The chiral vector is defined by Eq. (3.1), where n, m are integers $n \neq m$.

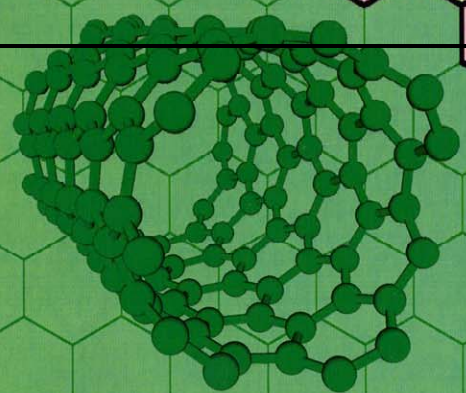
^{c)} The group theory of carbon nanotubes is discussed in Sect. 3.6.

Periodic Table of Carbon Nanotubes



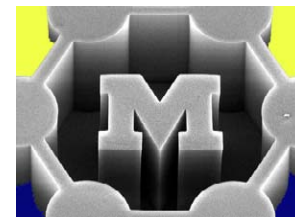
The semi-empirical bandgap E_g is calculated according to H. Yorikawa and S. Muramatsu, Phys. Rev. B 52, 2723 (1995) for the semiconducting tubes (no curvature effects) and A. Kleiner and S. Eggert, Phys. Rev. B 63, 073408 (2001) for the metallic and semi-metallic tubes (includes curvature). All other values are evaluated from the expressions below.

a_{C-C}	carbon-carbon distance		1.421 Å (graphite)
a	length of unit vector	$\sqrt{3} a_{C-C}$	2.461 Å
$\mathbf{a}_1, \mathbf{a}_2$	unit vectors	$\frac{a}{2}(\sqrt{3}, 1), \frac{a}{2}(\sqrt{3}, -1)$	in (x, y) coordinates
$\mathbf{b}_1, \mathbf{b}_2$	reciprocal unit vectors	$\frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 1), \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, -1)$	in (x, y) coordinates
\mathbf{C}_h	chiral vector	$n\mathbf{a}_1 + m\mathbf{a}_2$	n, m integer
L	circumference of tube	$L = \mathbf{C}_h = a\sqrt{n^2 + m^2 + nm}$	$0 \leq m \leq n$
d_t	diameter of tube	$d_t = L/\pi$	
θ	chiral angle	$\tan \theta = \frac{\sqrt{3}m}{2n+m}$	$0^\circ \leq \theta \leq 30^\circ$
d	highest common divisor of (n, m)		
d_R	highest common divisor of $(2n+m, 2m+n)$	$d_R = \begin{cases} d & \text{if } n-m \text{ is not a multiple of } 3d \\ 3d & \text{if } n-m \text{ is a multiple of } 3d \end{cases}$	
\mathbf{T}	translational vector of 1D unit cell	$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2$ $t_1 = (2m+n)/d_R$ $t_2 = -(2n+m)/d_R$	t_1, t_2 integer
T	length of \mathbf{T}	$T = \sqrt{3}L/d_R$	
N	number of atoms per 1D unit cell	$N = 4(n^2 + m^2 + nm)/d_R$	$N/2 =$ hexagons/unit cell

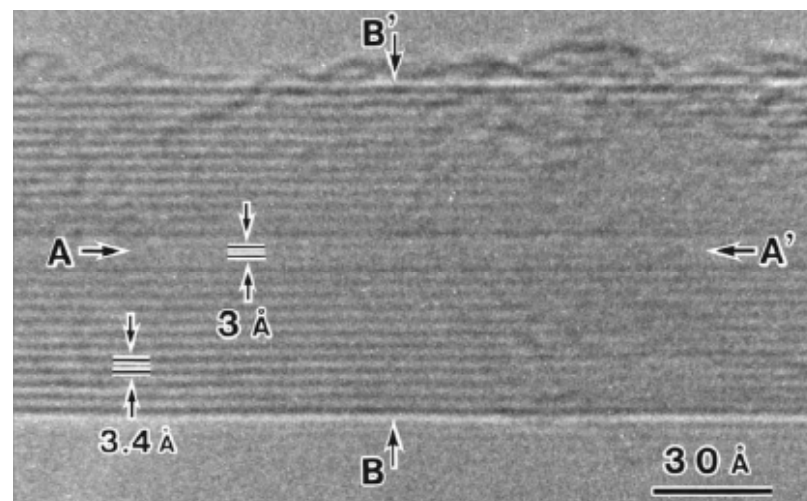
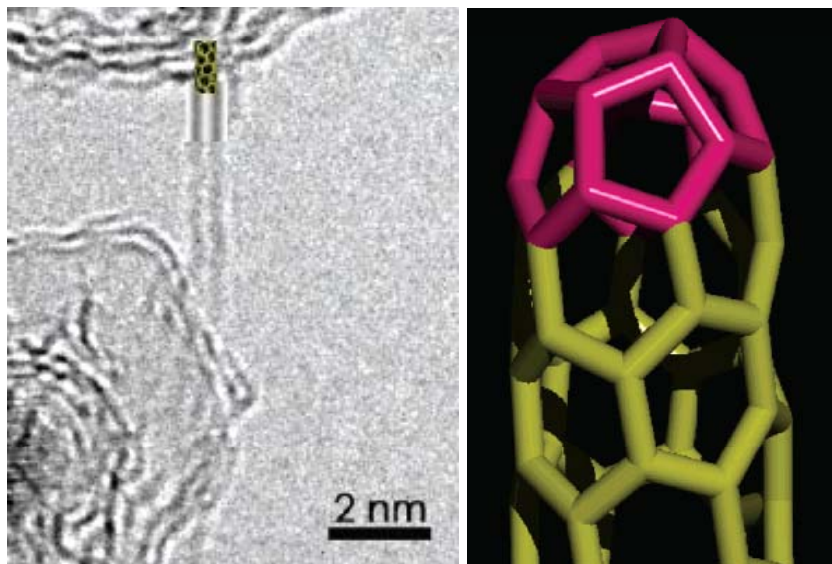


a_{C-C}	carbon-carbon distance		1.421 Å (graphite)
a	length of unit vector	$\sqrt{3} a_{C-C}$	2.461 Å
$\mathbf{a}_1, \mathbf{a}_2$	unit vectors	$\frac{a}{2}(\sqrt{3}, 1), \frac{a}{2}(\sqrt{3}, -1)$	in (x, y) coordinates
$\mathbf{b}_1, \mathbf{b}_2$	reciprocal unit vectors	$\frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 1), \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, -1)$	in (x, y) coordinates
\mathbf{C}_h	chiral vector	$n\mathbf{a}_1 + m\mathbf{a}_2$	n, m integer
L	circumference of tube	$L = \mathbf{C}_h = a\sqrt{n^2 + m^2 + nm}$	$0 \leq m \leq n$
d_t	diameter of tube	$d_t = L/\pi$	
θ	chiral angle	$\tan \theta = \frac{\sqrt{3}m}{2n+m}$	$0^\circ \leq \theta \leq 30^\circ$
d	highest common divisor of (n, m)		
d_R	highest common divisor of $(2n + m, 2m + n)$	$d_R = \begin{cases} d & \text{if } n - m \text{ is not a multiple of } 3d \\ 3d & \text{if } n - m \text{ is a multiple of } 3d \end{cases}$	
\mathbf{T}	translational vector of 1D unit cell	$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2$	t_1, t_2 integer
		$t_1 = (2m + n)/d_R$	
		$t_2 = -(2n + m)/d_R$	
T	length of \mathbf{T}	$T = \sqrt{3}L/d_R$	
N	number of atoms per 1D unit cell	$N = 4(n^2 + m^2 + nm)/d_R$	$N/2 = \text{hexagons/unit cell}$

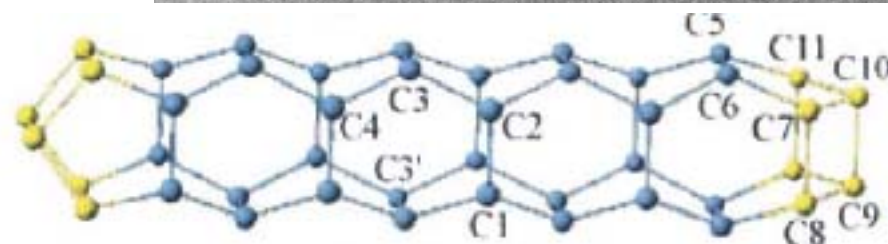
What is the smallest CNT?



4A



3A

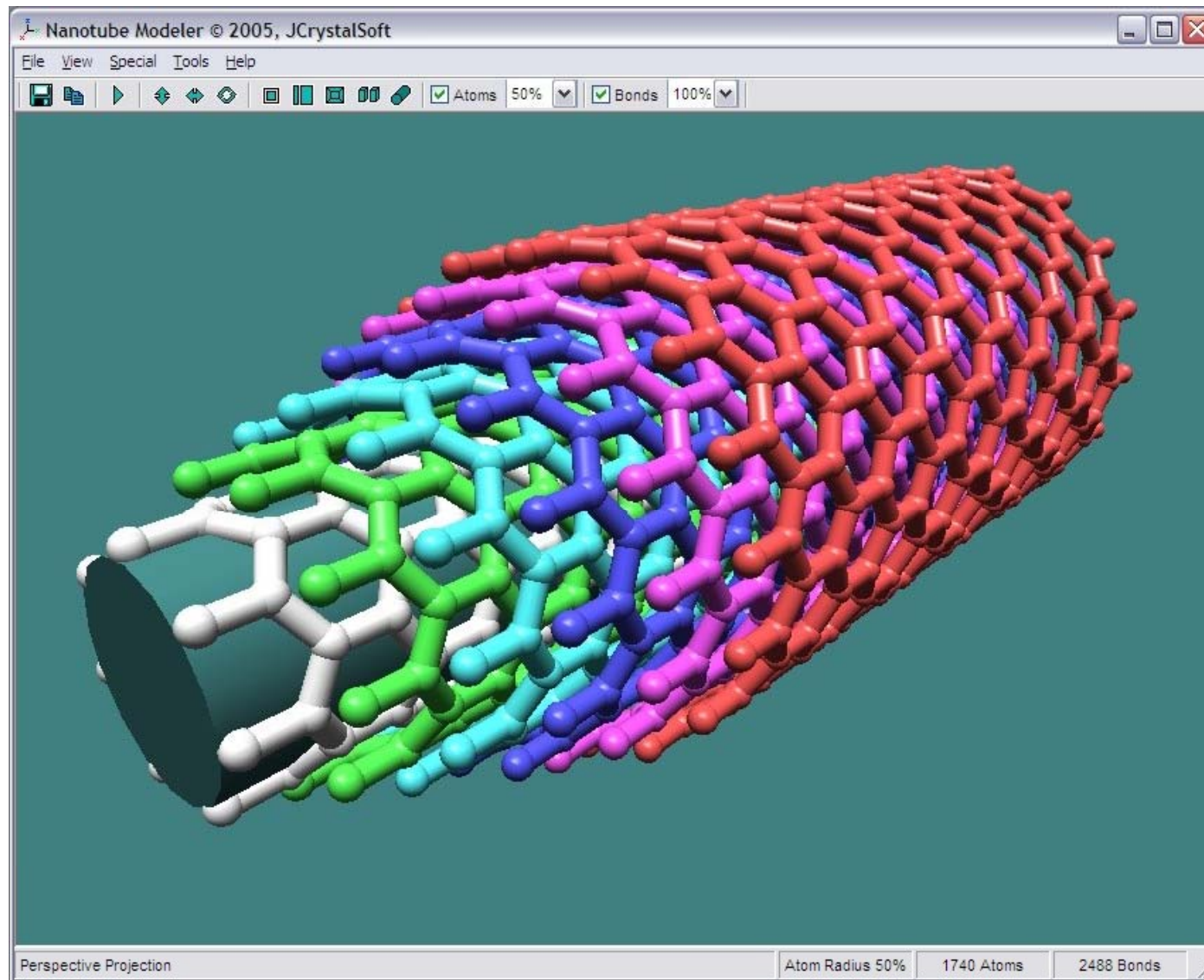
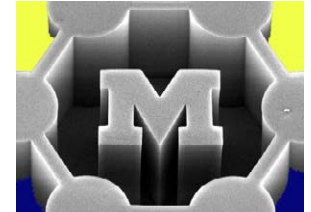


(d) 0.17 eV/atom

Hayashi et al., Nano Letters 3(7):887-889, 2003
Zhao et al., Phys Rev Lett 92(12):125502, 2004.

Nanotube modeler

<http://www.jcrystal.com/products/wincnt/>



Nanostructures are not always (pretty much never) perfect

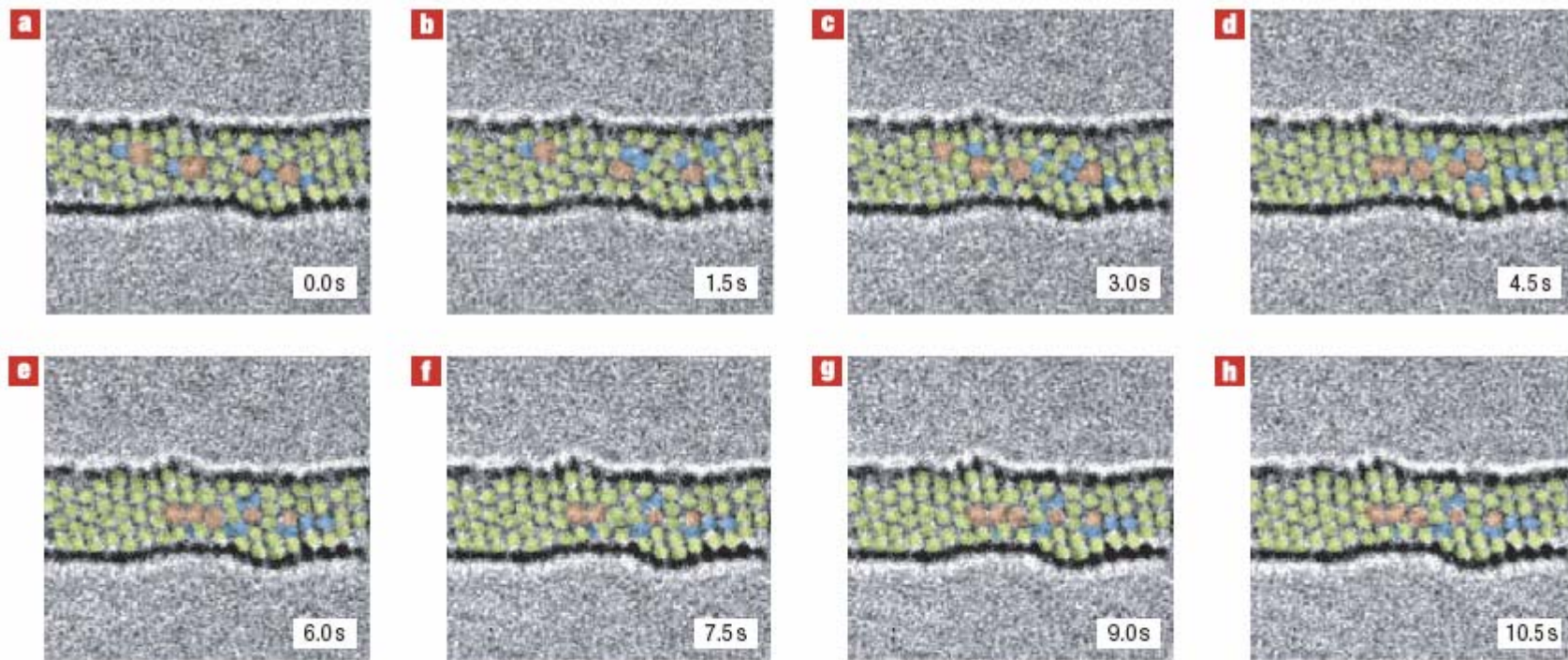
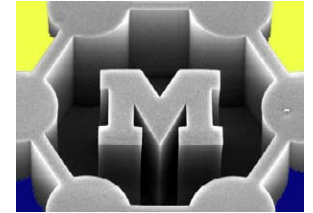


Figure 3 Active topological defects observed by *in situ* HR-TEM. a–h, Sequential HR-TEM images of an SWNT layer. Heptagons or higher-membered rings (red), hexagons (green) and pentagons or smaller rings (blue) of carbon atoms tend to gather around the kink structure during observations.