Optimal Functions and Nanomechanics III

APP MTH 3022/7106

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Lecture 11

Last lecture

- Extended the Euler-Lagrange equations to cases when the functional depends on multiple dependent variables.
- The Euler-Lagrange equations we derived were

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_k} - \frac{\partial L}{\partial q_k} = 0,$$

  for all $k = 1, \ldots, n$.
- We looked at a simple pendulum, the Brachistochrone in 3D, and planetary motion.
- We also Looked at Hamilton's principle of stationary action.

Nanomechanics

We take a slight detour to give a brief history and overview of nanotechnology and in particular nanomechanics.

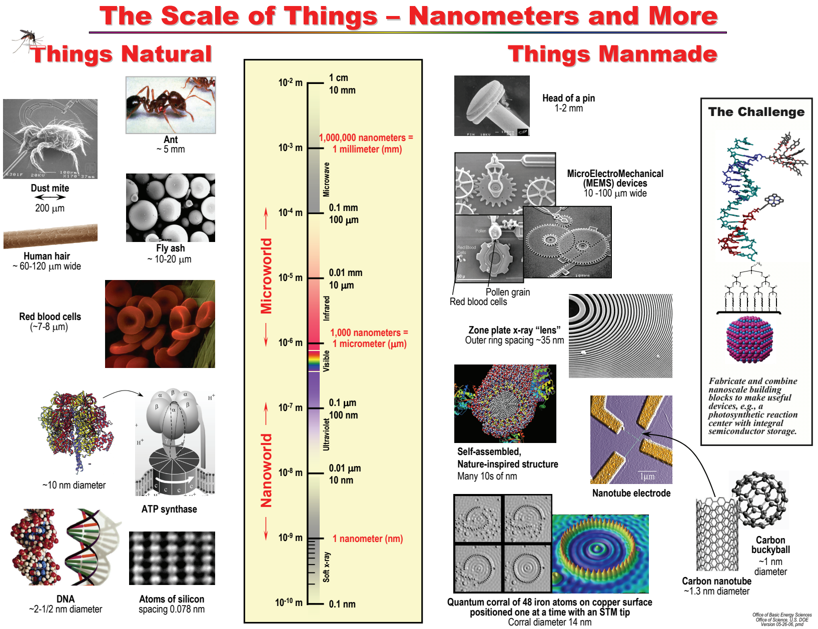
What is Nanotechnology?

Nanotechnology is the engineering of matter on the scale of individual atoms or small number of atoms. This might involve devices, materials, structures, or anything else where the length scale is important.

One **nanometre** (1 nm) is 10^{-9} of a metre.

One **angstrom** (1 Å) is 10^{-10} of a metre (that is, 0.1 nm).

Nanoscale is an imprecise term but usually refers to the scale from 1 Å to 100 nm.


The Scale of Things – Nanometers and More
Things Natural
Things Manmade
Dust mite
200 µm
Ant
~ 5 mm
Human hair
~ 60-120 µm wide
Fly ash
~ 10-20 µm
Red blood cells
(~7-8 µm)
~10 nm diameter
ATP synthase
DNA
~2-1/2 nm diameter
Atoms of silicon
spacing 0.078 nm
10^-2 m
1 cm
10 mm
10^-3 m
1,000,000 nanometers =
1 millimeter (mm)
Microwave
10^-4 m
0.1 mm
100 µm
Microworld
10^-5 m
0.01 mm
10 µm
Infrared
10^-6 m
1,000 nanometers =
1 micrometer (µm)
Visible
10^-7 m
0.1 µm
100 nm
Ultraviolet
Nanoworld
10^-8 m
0.01 µm
10 nm
10^-9 m
1 nanometer (nm)
Soft x-ray
10^-10 m
0.1 nm
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
Carbon nanotube
~1.3 nm diameter
Carbon buckyball
~1 nm
diameter
The Challenge
Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.
Office of Basic Energy Sciences
Office of Science, U.S. DOE
Version 05-26-06, pmd

Nanotechnology Timeline

1959 Feynman "There's plenty of room at the bottom"

1974 Taniguchi coins the term "nano-technology"

1977 Drexler popularises molecular nanotechnology

1981 Scanning Tunneling Microscope (STM) invented

1985 Curl, Kroto and Smalley discover fullerenes

1986 Atomic Force Microscope (AFM) invented

1991 Carbon nanotubes (re-)discovered by Iijima

1998 First DNA-based nanomechanical device

2004 Single sheet of graphene isolated by Geim and Novoselov

2007 First single carbon nanotube radio

Single Carbon Nanotube Radio

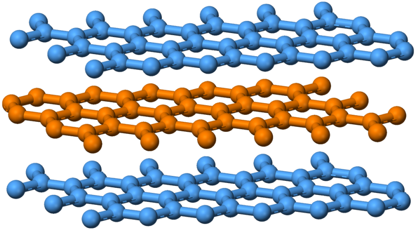
Structure of Graphite

Graphite is an allotrope of carbon comprising layers of carbon sheets covalently bonded in a hexagonal lattice.

The bonding between carbon atoms in the sheet is much stronger than the bonding between sheets.

The interatomic separation is approximately 1.42 Å.

The interlayer separation is approximately 3.35 Å.



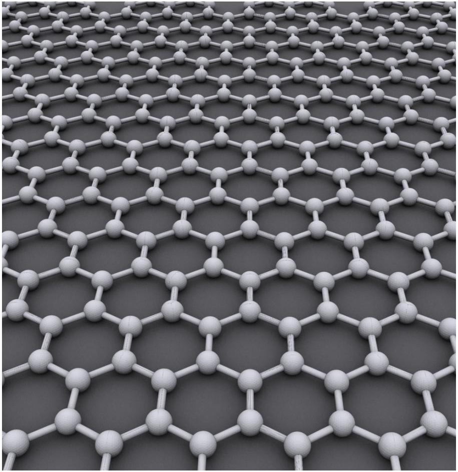
Structure of Graphene

Graphene describes a single sheet of graphitic carbon.

Originally though to be unstable as a single sheet, an individual sheet of graphene was first produced in 2004.

The interatomic separation is approximately 1.42 Å.

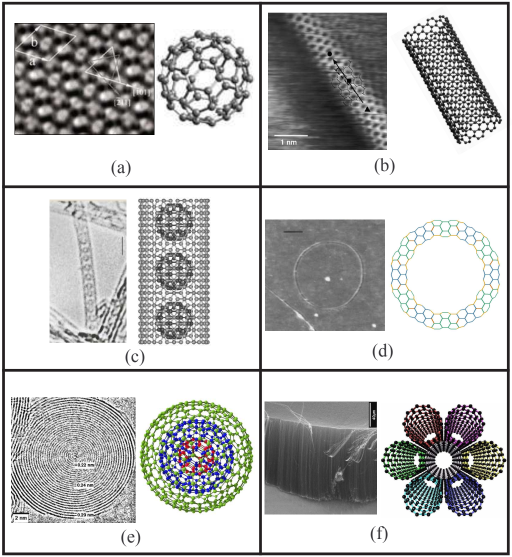
Graphene can be wrapped up into 0D fullerenes, rolled into 1D carbon nanotubes or stacked into 3D graphite.



Graphene-Based Nanostructures

There are a number of nanostructures that are based on graphene as their fundamental material. Some common examples are:

(a) Fullerene
(b) Carbon nanotube
(c) Nanopeapod
(d) Nanotorus
(e) Carbon onion
(f) Carbon nanotube bundle



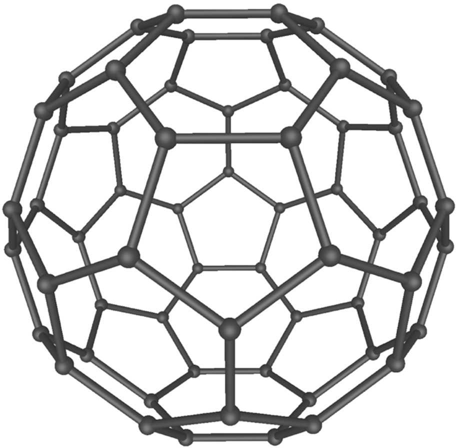
Fullerene

Fullerene describes a closed cage molecule comprised entirely of carbon.

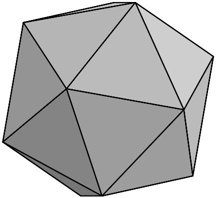
C_{60} fullerene comprises 60 carbon atoms and was discovered by Curl, Kroto and Smalley in 1985.

C_{60} is the smallest stable fullerene, with a radius of approximately 3.55 Å.

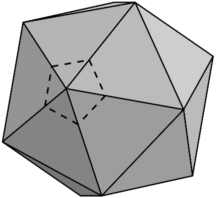
The atom positions are approximately the vertices of a **truncated icosahedron**.

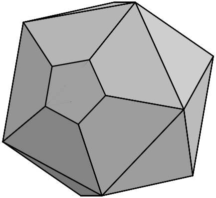


Truncating an Icosahedron

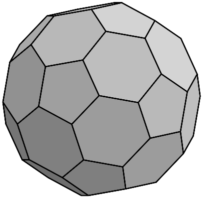


Icosahedron
20 triangular faces
30 edges
12 vertices





Truncated Icosahedron
20 hexagonal faces
12 pentagonal faces
90 edges
60 vertices

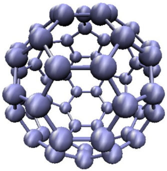


Spheroidal Fullerenes

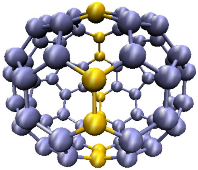
There are an infinite variety of fullerenes with various symmetries and isomers.

C_{70} fullerene is spheroidal and may be imagined as a C_{60} with 10 carbon atoms added around the equator.

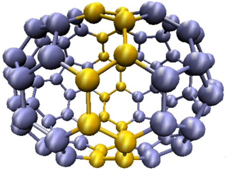
The C_{80} fullerene has seven known isomers, one of which can be thought of a C_{60} with 20 carbon atoms added around the equator.



C_{60}



C_{70}



C_{80}

Goldberg Fullerenes

Goldberg fullerenes have icosahedral symmetry.

They can be thought of as constructed from 20 congruent equilateral triangles, cut from a sheet of graphene with 12 pentagons at every vertex (where the triangles meet).

One side of the fundamental equilateral triangle is characterised by two integers (n, m) and the number of atoms N making up the fullerene is given by

$$N = 20(n^2 + nm + m^2).$$

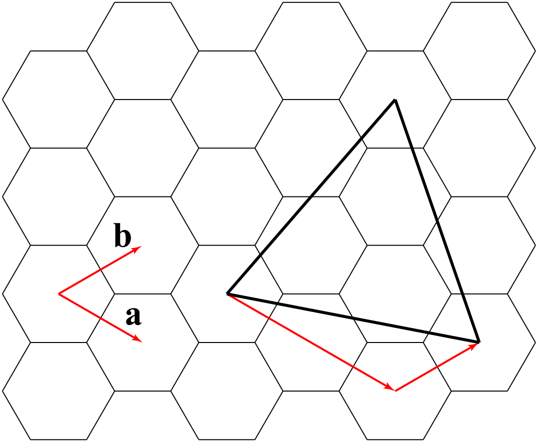
The C_{60} fullerene is an example of a Goldberg fullerene with $n = 1$ and $m = 1$.

Basis Vectors and Vector Numbers

Vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ provide a nonorthogonal basis for the hexagonal lattice.

The vector numbers (n, m) give the distance in the directions of $\boldsymbol{a}$ and $\boldsymbol{b}$, respectively

Given one side the other sides follow since the triangle is equilateral.



Shows a $(2, 1)$ triangle. N.B. the origin lies at the centre of a hexagonal ring.

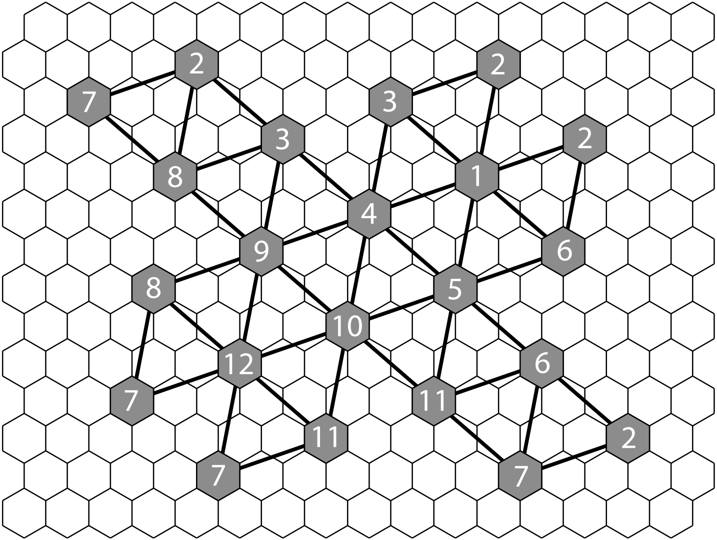
Constructing Goldberg Fullerenes

Generating icosahedral fullerenes is formulated using equilateral triangles as basic building blocks. An icosahedral fullerene consists of exactly twenty equilateral triangles, each specified by a pair of integers (n, m).

The twenty equilateral triangles which make up a fullerene consist of ten triangles in the **belt area** and five triangles in each of the two **cap regions**.

Note that the vertices of each triangle (on the next slide) are labelled with a number from 1 to 12, which refer to the pentagonal rings on the icosahedral fullerene.

Net of a Goldberg Fullerene $(2,1)$ C_{140}



Calculating the Number of Atoms N in Fullerene

The basis vectors can be written as

$$\boldsymbol{a} = \frac{3\sigma}{2}\boldsymbol{i} - \frac{\sqrt{3}\sigma}{2}\boldsymbol{j}, \quad \boldsymbol{b} = \frac{3\sigma}{2}\boldsymbol{i} + \frac{\sqrt{3}\sigma}{2}\boldsymbol{j},$$

where σ is the carbon-carbon bond length, and $\boldsymbol{i}$ and $\boldsymbol{j}$ are the usual Cartesian basis vectors. So the vector for the triangle side $\boldsymbol{C}$ is given by

$$\boldsymbol{C} = \frac{3\sigma}{2}(n+m)\boldsymbol{i} - \frac{\sqrt{3}\sigma}{2}(n-m)\boldsymbol{j}.$$

The norm of this vector is the side length s, given by

$$s = \|\boldsymbol{C}\| = \sqrt{3}\sigma(n^2 + nm + m^2)^{1/2}.$$

Calculating the Number of Atoms N in Fullerene

The area of an equilateral triangle is given by $A_\triangle = \sqrt{3}s^2/4$ and thus for our fundamental triangle we have

$$A_\triangle = 3\sqrt{3}\sigma^2(n^2 + nm + m^2)/4.$$

Each hexagon comprises six carbon atoms where each atom participates in three hexagons. So each hexagon contains two whole carbon atoms. $A_{hex} = 3\sqrt{3}\sigma^2/2$ is the area of one hexagon and so the number of atoms per side $N_\triangle$ is

$$N_\triangle = 2\frac{A_\triangle}{A_{hex}} = 2\frac{3\sqrt{3}\sigma^2(n^2 + nm + m^2)/4}{3\sqrt{3}\sigma^2/2} = n^2 + nm + m^2.$$

Now the total number of atoms N can be worked out from the number of faces of an icosahedron and is given by

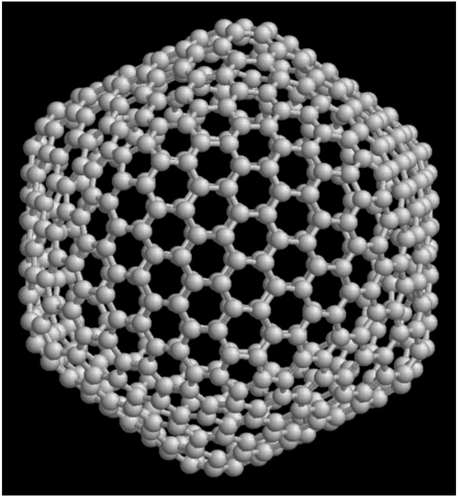
$$N = 20N_\triangle = 20(n^2 + nm + m^2).$$

The Radius of a Goldberg Fullerene

Strictly speaking a Goldberg fullerene is an icosahedron and not a sphere and so the shape should have both an in- and out-radius.However in practice it take more energy to bend bonds sharply and so the structure actually seen will be approximately spherical.

This leads to the question:

How might we approximate the radius of a Goldberg fullerene?



One Estimate for the Radius

One estimate can be made by looking at the map from the fullerene a few slides ago. The **belt region** comprises ten triangles and therefore has a length of $5s$, which is approximately equivalent to the circumference of the fullerene. Thus the radius $r \approx 5s/2\pi$. Expanding gives

$$r \approx \frac{5\sqrt{3}\sigma}{2\pi}(n^2 + nm + m^2)^{1/2}.$$

However a basis for the estimate of the radius might also be argued from the area of the icosahedron.

Another Estimate for the Radius

The area of the icosahedron is $A = 20A_{\triangle}$ and the the radius of a sphere with the same surface area would be given by $r \approx (A/4\pi)^{1/2}$. Substituting for the area of a triangle worked out previously we have

$$r \approx \frac{3^{3/4}\sqrt{5}\sigma}{2\sqrt{\pi}}(n^2 + nm + m^2)^{1/2}.$$

Both formulae give an approximation which varies by approximately 4 % but which is better?

The more accurate estimate is a matter for some debate. However, the first one is slightly simpler to calculate.

Euler's Theorem for Polyhedra

Leonhard Euler (1707-1783), the famous Swiss mathematician, proposed numerous theorems many of which are regularly used today. One of his theorems which relates to polyhedra can be used to describe the geometry of carbon structures. Euler's theorem is embodied in the equation

$$v - e + f = 2(1 - g)$$

where v, e and f are the number of vertices, edges and faces, respectively, and g is the genus of the polyhedron.

The **genus** can be thought of as the number of "handles" of the solid. Fullerenes have genus $g = 0$ and nanotori have a genus $g = 1$.

Cauchy's Proof of Euler's Theorem (for $g = 0$)

Idea: We make various transformations to the graph representing the polyhedron keeping track of the characteristic

$$\chi = v - e + f$$

Step 1: For any polyhedron of genus $g = 0$ we can map from the polyhedron to a graph without changing the number of vertices, edges or faces (the area outside of the graph is considered a face) and thus the characteristic χ remains unchanged.

Step 2: For every face which is not triangular, we add a line joining two vertices until all faces are triangular. Each additional edge increases e by 1 and increases f by one. Therefore the characteristic χ remains unchanged.

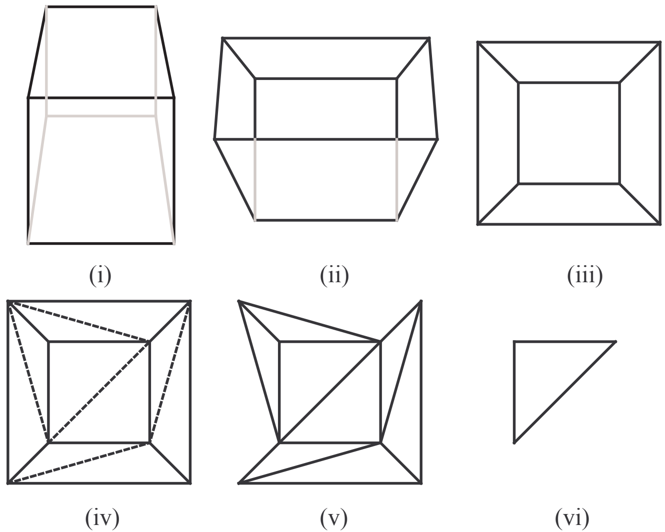
Cauchy's Proof of Euler's Theorem

Step 3: Now working from the outside of the graph, we remove triangles with only one external edge. This decreases e by one and decreases f by one. Therefore χ remains unchanged.

Step 4: Again working from the outside of the graph, we remove triangles with two external edges. This decreases e by two and decreases f by one, but also decreases v by one, and once again, χ remains unchanged.

Step 5: We repeat Steps 3 and 4 until there is just one triangle left. This final graph has $v = 3$, $e = 3$ and $f = 2$ (remembering that the area outside of the graph is a face) and hence $\chi = 2$. Since none of the steps changed the value of χ, our original polyhedron must have also had $\chi = 2.\square$

Cauchy's Proof of Euler's Theorem



Number of Pentagons in a Fullerene

Assuming that the fullerene is homomorphic to a sphere (genus zero) then Euler's theorem becomes

$$v - e + f = 2.$$

Now assuming the fullerene contains only pentagonal and hexagonal rings, we denote the number of pentagons by p and the number of hexagons h, and further we assume that every atom (vertex) in the fullerene is bonded to three neighbours then we can derive the following relations

$$f = p + h, \quad v = \frac{5p + 6h}{3}, \quad e = \frac{5p + 6h}{2}.$$

Number of Pentagons in a Fullerene

Substituting these three equations into Euler's theorem we obtain

$$\frac{5p+6h}{3} - \frac{5p+6h}{2} + p + h = 2,$$
$$10p + 12h - 15p - 18h + 6p + 6h = 12,$$

which may be simplified to

$$p = 12.$$

Thus for such fullerenes, no matter the size, there may be any number of hexagons but always precisely 12 pentagons.

This remarkable results also holds for any surface of genus zero. For example, capped carbon nanotubes requires precisely six pentagons to close each end.