Optimal Functions and Nanomechanics III

APP MTH 3022/7106

Barry Cox

Lecture 12

Last lecture

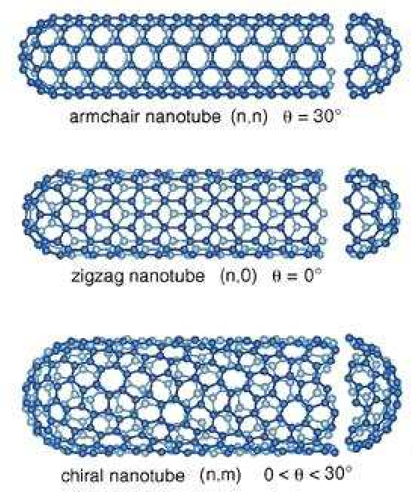
- Had a brief history/introduction to nanoscience
- Looked at Graphite, graphene and graphitic nanostructures
- Saw how to calculate the radius and mass of Goldburg fullerenes
- Used Euler's formula to prove that fullerenes have exactly twelve pentagons

Carbon Nanotubes

Carbon nanotube describes a macromolecule comprised entirely of carbon which has a cylindrical shape.

Nanotubes can be closed cage molecules if the cylinder is capped. Alternatively a nanotube may be uncapped exposing the interior surface for interaction.

The **chirality** of a nanotube refers to the alignment of the hexagons around the cylinder.



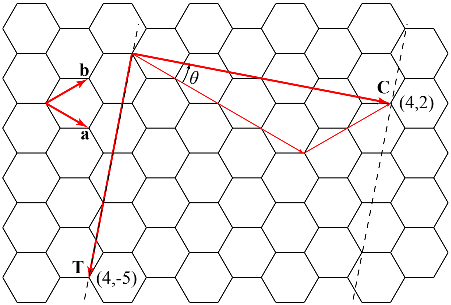
Chirality of Carbon Nanotubes

The chirality is described by the chiral vector $\boldsymbol{C}$, which is defined by $\boldsymbol{C} = n\boldsymbol{a} + m\boldsymbol{b}$, or also written as (n, m) which are known as the **chiral vector numbers**.

By convention, $0 \leqslant m \leqslant n$.

The angle between $\boldsymbol{a}$ and $\boldsymbol{C}$ is denoted by θ and called the **chiral angle**.

Perpendicular to $\boldsymbol{C}$ is the **translation vector** $\boldsymbol{T}$.



The example above shows a $(4, 2)$ chiral vector. N.B. the origin lies at a lattice point.

Rolled-up Model for Carbon Nanotubes

The rolled up model for carbon nanotubes assumes that the graphene plane my be sliced (along the dashed lines) and rolled into a perfect right-circular cylinder. The chiral angle θ is an important parameter and given by

$$\theta = \cos^{-1}\left(\frac{2n+m}{2\sqrt{n^2+nm+m^2}}\right).$$

There are three general cases:

1. $m = 0$ give **zigzag** nanotubes with $\theta = 0$.
2. $0 < m < n$ give **chiral** nanotubes with $0 < \theta < \pi/6$.
3. $m = n$ give **armchair** nanotubes with $\theta = \pi/6$.

All nanotubes can be represented by a chiral angle in the range $0 \leqslant \theta \leqslant \pi/6$.

Nanotube Radius

In the rolled-up model the chiral vector $\boldsymbol{C}$ is transformed into a circumference of the cylinder. Hence the radius of the nanotubes r is given by $r = |\boldsymbol{C}|/2\pi$. From earlier

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

Substitution gives

$$|\boldsymbol{C}| = \sigma \left[\frac{9}{4}(n+m)^2 + \frac{3}{4}(n-m)^2\right]^{1/2} = \sigma\sqrt{3(n^2+nm+m^2)},$$

and hence the radius is given by

$$r = \frac{\sigma\sqrt{3(n^2+nm+m^2)}}{2\pi}.$$

Translation Vector

The translation vector $\boldsymbol{T}$ is perpendicular to the chiral vector and gives the distance along the tube axis between atoms which are equivalent and vary only by only a translation in the axial direction.

This is considered a unit cell of the carbon nanotube.

$$\boldsymbol{T} = \frac{n+2m}{d_R}\boldsymbol{a} - \frac{2n+m}{d_R}\boldsymbol{b},$$

where d_R is the greatest common divisor of the two numerators. That is

$$d_R = \gcd(n+2m, 2n+m).$$

Nanotube Unit Cell

The rectangle defined by the vectors $\boldsymbol{C}$ and $\boldsymbol{T}$ give the unit cell for a particular carbon nanotube. The length of the translation vector is given by

$$\|\boldsymbol{T}\| = 3\sigma\sqrt{n^2 + nm + m^2}/d_R,$$

and so the area of the unit cell is

$$A = \|\boldsymbol{C}\| \cdot \|\boldsymbol{T}\| = 3\sqrt{3}\sigma^2(n^2 + nm + m^2)/d_R.$$

From earlier the area of a hexagon is $A_{hex} = 3\sqrt{3}\sigma^2/2$ and therefore the number of hexagons N_{hex} in a unit cell is

$$N_{hex} = A/A_{hex} = 2(n^2 + nm + m^2)/d_R,$$

and each hexagon contains 2 whole atoms $(6 \times 1/3)$ and so the number of atoms N in a unit cell is

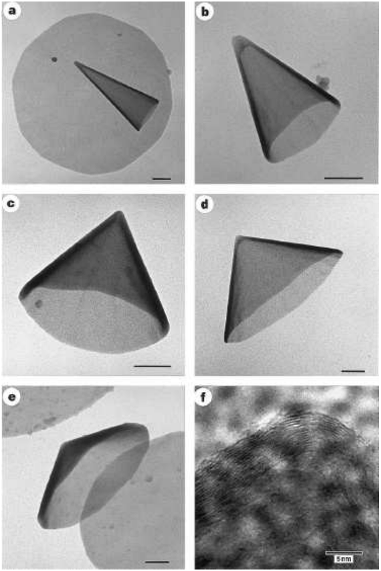
$$N = 2N_{hex} = 4(n^2 + nm + m^2)/d_R.$$

Carbon Nanocones

Carbon nanocone describes a macromolecule comprised entirely of carbon which has a conical shape.

Unlike nanotubes, nanocones are always open at one end and usually capped at the other.

The nanocones don't have a chirality but the **open angle** varies depending on the number of pentagons forming the cap.



Nanocone Structure

Nanocones are formed from hexagons on a honeycombed lattice by adding fewer pentagons than the six which are needed by Euler's theorem to form the closed structure of a semi-fullerene.

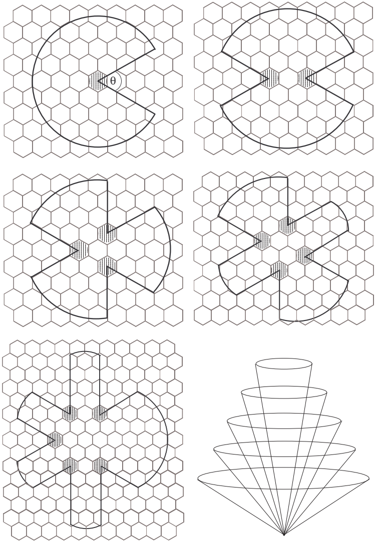
The carbon nanotube cap, which is half a fullerene or semi-fullerene, contains six pentagons, and therefore carbon nanocones must have a number of pentagons which is less than six.

Therefore there are five different nanocones structures which vary in the open angle at the tip of the cone.

Nanocone Construction

Construction of cones by creation of disclinations (triangular wedges) in the graphene lattice. The part of the graphene plane bounded by the thick lines is folded into a cone.

Here we see the graphene cut-outs used to construct the cones with one, two, three, four and five pentagons, respectively (shaded hexagons become pentagons when forming cones).



Nanocone Open Angle α

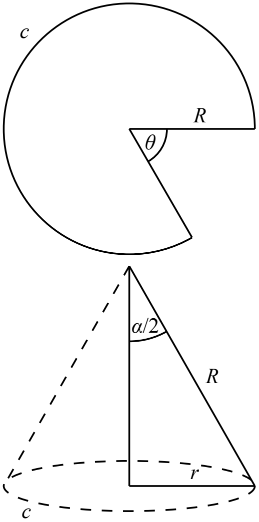
The disclination number of pentagons N_p on the graphene sheet gives the change with θ in the form

$$\theta = \pi N_p/3.$$

It is clear that $\sin(\alpha/2) = r/R$ and $c = 2\pi r = 2\pi(1 - N_p/6)R$.

Therefore, the relation of the cone angle and the number of pentagons is obtained as

$$\sin(\alpha/2) = 1 - \frac{N_p}{6}.$$



Nanocone Angle Values

There are five possible values of the open angle α depending on the number of pentagons N_p. When $N_p = 0$ we have a flat graphene sheet and when $N_p = 6$ we have the cap of a carbon nanotube.

Relationship between the number of pentagons N_p and the open angle α for carbon nanocones.

Number of pentagons N_p	Open Angle α
1	112.89°
2	83.62°
3	60.00°
4	38.94°
5	19.19°

The Gamma Function: $\Gamma(z)$

For $\Re(z) > 0$ the gamma function $\Gamma(z)$, can be defined by the definite integral

$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt,$$

which is known as the Euler integral form. Integrating $\Gamma(z+1)$ by parts yields

$$\Gamma(z+1) = \int_0^\infty t^z e^{-t} dt = \left[-t^z e^{-t}\right]_0^\infty + z \int_0^\infty t^{z-1} e^{-t} dt,$$

and we observe that the first term is zero and that the second term is simply $z\Gamma(z)$. This allows us to write the basic recurrence relationship for the gamma function

$$\boxed{\Gamma(z+1) = z\Gamma(z).}$$

The Gamma Function: $\Gamma(z)$

It can be seen from the recurrence relationship, and the fact that $\Gamma(1) = 1$, that when z is a positive integer n, the gamma function corresponds closely to the factorial operator given by the expression

$$\boxed{\Gamma(n+1) = n!}$$

For certain values of z the Euler integral form has singularities (e.g. at non-positive integers). However we may replace the non-analytical Euler integral form of the gamma function with a function and an integral which is well-defined for all values of z.

$$\begin{aligned}\Gamma(z) = \int_0^\infty t^{z-1}e^{-t}dt &= \int_0^1 t^{z-1}e^{-t}dt + \int_1^\infty t^{z-1}e^{-t}dt \\ &= P(z) + \int_1^\infty t^{z-1}e^{-t}dt.\end{aligned}$$

Recurrence relationship

Expanding e^{-t} as a power series and integrating term by term gives

$$P(z) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!(z+n)},$$

and therefore

$$\Gamma(z) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!(z+n)} + \int_1^{\infty} t^{z-1}e^{-t}dt.$$

The final integral term is analytic for all z, and we can see from the sum that the gamma function is always analytic except at the points $z = 0, -1, -2, \ldots$ and at $z = -n$, the gamma function has simple poles with residues of $(-1)^n/n!$.

Identities for the Gamma Function

The gamma function is analytic everywhere in the complex plane except for the points $z = 0, -1, -2, \ldots$ and it satisfies the following functional identity

$$\boxed{\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin(\pi z)},}$$

which relates the gamma function to the trigonometric functions. The gamma function also satisfies the well-known duplication formula

$$\boxed{\Gamma(2z) = 2^{2z-1}\pi^{-1/2}\Gamma(z)\Gamma(z+1/2),}$$

which is due to Legendre.

Identities for the Gamma Function

The duplication formula can be extended to the general multiplication formula, given by

$$\boxed{\prod_{\ell=0}^{m-1} \Gamma(z + \ell/m) = (2\pi)^{(m-1)/2} m^{1/2-mz} \Gamma(mz),}$$

where $m = 2, 3, 4, \ldots$ and where $\prod$ denotes the product of a sequence of terms such that

$$\prod_{\ell=m}^{n} x_\ell = x_m \cdot x_{m+1} \cdot x_{m+2} \cdot \cdots \cdot x_{n-1} \cdot x_n.$$

For example, for $m = 3$ the multiplication formula gives

$$\Gamma(z)\Gamma(z + 1/3)\Gamma(z + 2/3) = 2\pi 3^{1/2-3z} \Gamma(3z).$$

Example 1

Example: Show that $\Gamma(1/2) = \sqrt{\pi}$ using Euler integral form.

Solution: Substitution $z = 1/2$ into the definition we obtain

$$\Gamma(1/2) = \int_0^\infty \frac{e^{-u}}{\sqrt{u}} du = \int_0^\infty \frac{e^{-v}}{\sqrt{v}} dv,$$

and hence taking the square yields

$$\Gamma^2(1/2) = \int_0^\infty \frac{e^{-u}}{\sqrt{u}} du \int_0^\infty \frac{e^{-v}}{\sqrt{v}} dv.$$

Making the substitutions $u = x^2$ and $v = y^2$ gives

$$\Gamma^2(1/2) = 4 \int_0^\infty \int_0^\infty e^{-(x^2+y^2)} dx\, dy.$$

Example 1

We have obtained an integral in the form of a surface integral in the quarter plane. Transforming to polar coordinates ($x = r\cos\theta$, $y = r\sin\theta$) we obtain

$$\begin{aligned}
\Gamma^2(1/2) &= 4\int_0^\infty \int_0^{\pi/2} re^{-r^2}\,d\theta\,dr \\
&= 2\pi \int_0^\infty re^{-r^2}\,dr \\
&= 2\pi \left[-\frac{e^{-r^2}}{2}\right]_0^\infty \\
&= \pi,
\end{aligned}$$

and taking the square root of both sides we obtain

$$\Gamma(1/2) = \sqrt{\pi}.$$

The Beta Function: $B(x, y)$

Closely related to the gamma function, the beta function satisfies the identity

$$\boxed{B(x, y) = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)}.}$$

When x, y are nonnegative integers we have

$$B(x+1, y+1) = \frac{x!y!}{(x+y+1)!} = \left[(x+y+1)\binom{x+y}{x}\right]^{-1}.$$

Integral forms

For $\Re(x), \Re(y) > 0$, the beta function is defined by the integral

$$\boxed{B(x,y) = \int_0^1 t^{x-1}(1-t)^{y-1}dt.}$$

If we make the substitution $t = \sin^2\theta$, so that $dt = 2\sin\theta\cos\theta\, d\theta$, we derive the useful

$$B(x,y) = 2\int_0^{\pi/2} \sin^{2x-1}\theta\cos^{2y-1}\theta\, d\theta.$$

Example 2

Example: Derive an expression for $\int_{-\pi/2}^{\pi/2} \cos^{2n}\theta\, d\theta$, ($n$ a natural number) terms of factorials.

Solution: From the result on the previous page

$$\begin{aligned}\int_{-\pi/2}^{\pi/2} \cos^{2n}\theta\, d\theta &= 2\int_0^{\pi/2} \cos^{2n}\theta\, d\theta \\ &= B(n+1/2, 1/2) \\ &= \frac{\Gamma(n+1/2)\Gamma(1/2)}{\Gamma(n+1)}.\end{aligned}$$

We know $\Gamma(1/2) = \pi^{1/2}$ and from the duplication formula we have

$$\Gamma(n+1/2) = \frac{\pi^{1/2}\Gamma(2n)}{2^{2n-1}\Gamma(n)}.$$

Example 2

Therefore

$$\int_{-\pi/2}^{\pi/2} \cos^{2n}\theta \, d\theta = \frac{\pi\Gamma(2n)}{2^{2n-1}\Gamma(n)\Gamma(n+1)}.$$

and multiplying top and bottom by $2n$ we have

$$\begin{aligned}\int_{-\pi/2}^{\pi/2} \cos^{2n}\theta \, d\theta &= \frac{\pi\Gamma(2n+1)}{2^{2n}\Gamma^2(n+1)} \\ &= \frac{\pi(2n)!}{2^{2n}(n!)^2}.\end{aligned}$$

The Pochhammer Symbol: $(a)_n$

The Pochhammer symbol was introduced by Leo August Pochhammer (1841-1920), a Prussian mathematician known for his work on special functions. This is denoted by $(a)_n$ and is defined by

$$(a)_n = a(a+1)(a+2)\cdots(a+n-1).$$

If the argument a is an integer then we can write

$$(a)_n = \frac{(a+n-1)!}{(a-1)!},$$

and this can be extended to include non-integer and complex values of a by the definition

$$\boxed{(a)_n = \frac{\Gamma(a+n)}{\Gamma(a)}.}$$

Example 3

Example: Derive an expression for $(-n)_m$ where $n = 1, 2, 3, \ldots$, in terms of factorials.

Solution: From the definition of the Pochhammer symbol we have

$$\begin{aligned}
(-n)_m &= (-n)(1-n)(2-n)\cdots(m-n-1) \\
&= (-1)^m n(n-1)(n-2)\cdots(n-m+1) \\
&= (-1)^m \frac{n!}{(n-m)!},
\end{aligned}$$

therefore

$$(-n)_m = \begin{cases} \dfrac{(-1)^m n!}{(n-m)!}, & m \leqslant n, \\ 0, & m > n. \end{cases}$$

The Hypergeometric Function: $F(a, b; c; z)$

Evaluation of the interaction energy between two molecular structures having well-defined shapes such as cylinders, spheres and cones generally leads to hypergeometric functions. The hypergeometric function has a series definition given by

$$\boxed{F(a, b; c; z) = \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n} \frac{z^n}{n!},}$$

and has the integral representation

$$F(a, b; c; z) = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \int_0^1 t^{b-1}(1-t)^{c-b-1}(1-tz)^{-a} dt,$$

for $\Re(c) > \Re(b) > 0$.

Relationships to elementary functions

Several of the elementary functions can be given in terms of hypergeometric functions including:

$$
\begin{aligned}
(1+z)^a &= F(-a, b; b; -z), \\
\sin^{-1}(z) &= zF(1/2, 1/2; 3/2; z^2), \\
\sinh^{-1}(z) &= zF(1/2, 1/2; 3/2; -z^2), \\
\tan^{-1}(z) &= zF(1/2, 1; 3/2; -z^2), \\
\tanh^{-1}(z) &= zF(1/2, 1; 3/2; z^2), \\
\log(1+z) &= zF(1, 1; 2; -z).
\end{aligned}
$$

Note that in this course, the function $\log(z)$ will always refer to the natural logarithm.

Properties

From the series definition of the hypergeometric function

$$F(a, b; c; z) = \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n} \frac{z^n}{n!},$$

and what we know about the Pochhammer symbol, we can make the following observations:

- if either a or b is a negative integer then the series terminates after a finite number of terms;
- if c is a negative integer then the series becomes undefined after a finite number of terms;
- the ratio of successive terms approaches z in the limit as $n \to \infty$; and thus
- the series is absolutely convergent for $|z| < 1$.

Relationships to the orthogonal polynomials

Many of the classical families of orthogonal polynomials can be expressed as terminating hypergeometric series, such as

$$
\begin{aligned}
T_n(x) &= F(-n, n; 1/2; (1-x)/2), \\
U_n(x) &= (n+1)F(-n, n+2; 3/2; (1-x)/2), \\
P_n(x) &= F(-n, n+1; 1; (1-x)/2),
\end{aligned}
$$

where $T_n(x)$ and $U_n(x)$ denote the Chebyshev polynomials of the first and second kind, and $P_n(x)$ denotes the Legendre polynomials.