

Optimal Functions and Nanomechanics III

APP MTH 3022/7106

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Lecture 13

Last lecture

- Defined the chirality of carbon nanotubes
- Briefly introduced carbon nanocones.
- Introduced some special functions
 - Gamma function $\Gamma(z)$
 - The closely related Beta function $B(x, y)$
 - Usual hypergeometric function $F(a, b; c; z)$
- We also saw some new notation in the Pochhammer symbol where

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

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

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

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:

$$(1+z)^a = F(-a, b; b; -z),$$

$$\sin^{-1}(z) = zF(1/2, 1/2; 3/2; z^2),$$

$$\sinh^{-1}(z) = zF(1/2, 1/2; 3/2; -z^2),$$

$$\tan^{-1}(z) = zF(1/2, 1; 3/2; -z^2),$$

$$\tanh^{-1}(z) = zF(1/2, 1; 3/2; z^2),$$

$$\log(1+z) = zF(1, 1; 2; -z).$$

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 $n \rightarrow \infty$; 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

$$T_n(x) = F(-n, n; 1/2; (1-x)/2),$$

$$U_n(x) = (n+1)F(-n, n+2; 3/2; (1-x)/2),$$

$$P_n(x) = F(-n, n+1; 1; (1-x)/2),$$

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.

Hypergeometric Differential Equation

Differentiation of the hypergeometric function is straightforward and the n^{th} derivative is given by

$$\frac{d^n}{dz^n} F(a, b; c; z) = \frac{(a)_n (b)_n}{(c)_n} F(a + n, b + n; c + n; z).$$

The hypergeometric function is a solution of a homogeneous linear second order differential equation, with regular singularities at $z = 0$, 1 and ∞ . This is called the hypergeometric equation and is given by

$$z(1 - z) \frac{d^2 u}{dz^2} + [c - (a + b + 1)z] \frac{du}{dz} - abu = 0,$$

where a , b and c are independent of z .

Any second order linear ordinary differential equation with at most three regular singular points can be transformed into the hypergeometric equation.

It follows that $u_1 = F(a, b; c; z)$ is a solution of this differential equation that is regular at $z = 0$.

The second solution can depend on the values of the parameters a , b and c and relationships between them due to certain degenerate cases. However for the purpose of this course we will be much more interested in the hypergeometric function as defined from the integral form than solving the hypergeometric equation.

Quadratic Transformations

If and only if the six numbers

$$\pm(1 - c), \quad \pm(a - b), \quad \pm(a + b - c),$$

are such that one of them equals $1/2$ or two of them are equal, then there exists higher order transformations which are known as quadratic transformations.

The fundamental formulæ

$$\begin{aligned}
 F\left(a, b; 2b; \frac{4z}{(1+z)^2}\right) &= (1+z)^{2a} F\left(a, a-b+\frac{1}{2}; b+\frac{1}{2}; z^2\right), \\
 F(a, b; a-b+1; z) &= \\
 &\quad (1-z)^{-a} F\left(\frac{a}{2}, \frac{a+1}{2}-b; b-a+1; -4z(1-z^2)\right), \\
 F\left(a, a+\frac{1}{2}; b; z\right) &= 2^{2a} [1+(1-z)^{1/2}]^{-2a} \times \\
 &\quad F\left(2a, 2a-b+1; b; \frac{1-(1-z)^{1/2}}{1+(1-z)^{1/2}}\right), \\
 F\left(2a, 2b; a+b+\frac{1}{2}; z\right) &= F\left(a, b; a+b+\frac{1}{2}; 4z(1-z)\right),
 \end{aligned}$$

which are due to Gauss and Kummer.

Useful quadratic transformations

Some quadratic transformations which are particularly useful are

$$F(a, b; 2b; z) = (1 - z)^{a/2} F\left(a, 2b - a; b + \frac{1}{2}; -\frac{(1 - \sqrt{1 - z})^2}{4\sqrt{1 - z}}\right),$$

$$F(a, b; 2b; z) = \left(\frac{1 + \sqrt{1 - z}}{2}\right)^{-2a} \times \\ F\left(a, a - b + \frac{1}{2}; b + \frac{1}{2}; \left(\frac{1 - \sqrt{1 - z}}{1 + \sqrt{1 - z}}\right)^2\right).$$

However, there are many other formula which can be found in the reference texts. See for example Higher Transcendental Functions, Volumes I-III available online at

<http://resolver.caltech.edu/CaltechAUTHORS:20140123-104529738>.

Integral forms of the hypergeometric function

There are several integrals which define or involve the hypergeometric functions, and here we will include only the most useful ones.

Euler's integral formula is given by

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

provided that $\Re(c) > \Re(b) > 0$. There are also the closely related

$$F(a, b; c; 1-z) = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \int_0^\infty s^{b-1} (1+s)^{a-c} (1+sz)^{-a} ds,$$

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

Integral forms of the hypergeometric function

$$F\left(a, b; c; \frac{1}{z}\right) = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \int_1^\infty s^{a-c}(s-1)^{c-b-1} \left(s - \frac{1}{z}\right)^{-a} ds,$$

when $1 + \Re(a) > \Re(c) > \Re(b)$.

These integrals can be converted to trigonometric, hyperbolic or exponential functions by substitution of variables. It is interesting to note that in none of these integrals is the symmetry in a and b inherent in the relation $F(a, b; c; z) = F(b, a; c; z)$ readily apparent. Although this relationship is trivially apparent from the series representation.

Integral forms of the hypergeometric function

Motivated by this the following double integral identity

$$F(a, b; c; z) = \frac{(\Gamma(c))^2}{\Gamma(a)\Gamma(c-a)\Gamma(b)\Gamma(c-b)} \times \int_0^1 \int_0^1 \frac{t^{b-1} \tau^{a-1} (1-t)^{c-b-1} (1-\tau)^{c-a-1}}{(1-t\tau z)^c} dt d\tau,$$

was derived by Erdélyi in which the symmetry is obvious.

Appell's Hypergeometric f'n: $F_1(a, b, b'; c; x, y)$

The Appell's hypergeometric equation is a formal extension of the hypergeometric equation for two variables. The most commonly used form of the Appell's hypergeometric function is given by

$$F_1(a; b, b'; c; x, y) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(a)_{m+n} (b)_m (b')_n}{m! n! (c)_{m+n}} x^m y^n,$$

which is convergent for $|x| < 1$ and $|y| < 1$. The integral for for this function is given by

$$F_1 = \frac{\Gamma(c)}{\Gamma(a)\Gamma(c-a)} \int_0^1 t^{a-1} (1-t)^{c-a-1} (1-tx)^{-b} (1-ty)^{-b'} dt.$$

Other Appell's Hypergeometric functions

In fact there are four Appell's functions, and the remaining three, as defined by their expansions are

$$F_2(a; b, b'; c, c'; x, y) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(a)_{m+n} (b)_m (b')_n}{m! n! (c)_m (c')_n} x^m y^n,$$

$$F_3(a, a'; b, b'; c; x, y) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(a)_m (a')_n (b)_m (b')_n}{m! n! (c)_{m+n}} x^m y^n,$$

$$F_4(a; b; c, c'; x, y) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(a)_{m+n} (b)_{m+n}}{m! n! (c)_m (c')_n} x^m y^n.$$

There are various transformations of the Appell's hypergeometric function which enable this more complicated hypergeometric function to be simplified to ordinary hypergeometric functions.

Some transformations

For example, we can see from the series definitions that

$$\begin{aligned}F_1(a; b, b'; c; x, 0) &= F(a, b; c; x), \\F_1(a; b, b'; c; 0, y) &= F(a, b'; c; y).\end{aligned}$$

It is also possible to transform Appell's functions into other Appell's functions, and one such transformation which is useful is

$$F_1(a; b, b'; c; x, y) = (1 - y)^{-a} F_1 \left(a; b, c - b - b'; c; \frac{y - x}{y - 1}, \frac{y}{y - 1} \right),$$

and the equivalent

$$F_1(a; b, b; c; x, y) = (1 - y)^{-a} F_1 \left(a; b, c - 2b; c; \frac{y - x}{y - 1}, \frac{y}{y - 1} \right).$$

Some transformations

Another useful transformation which enables the Appell's hypergeometric function to be expressed in terms of an infinite sum of ordinary hypergeometric functions is

$$F_1(a; b, b'; c; x, y) = \sum_{m=0}^{\infty} \frac{(a)_m (b)_m}{m! (c)_m} F(a + m, b'; c + m; y) x^m.$$

This representation turns out to be useful for computational purposes in mathematical packages (such as MAPLE and MATLAB) which have implemented the usual hypergeometric function but not Appell's hypergeometric function.

Elliptic Integrals: $F(\varphi, k)$, $E(\varphi, k)$

The fundamental forms of the normal elliptic integrals of the first and second kind are

$$F(\varphi, k) = \int_0^\varphi \frac{d\vartheta}{\sqrt{1 - k^2 \sin^2 \vartheta}},$$
$$E(\varphi, k) = \int_0^\varphi \sqrt{1 - k^2 \sin^2 \vartheta} d\vartheta.$$

where we have adopted Legendre's notation and $0 \leq \varphi \leq \pi/2$, is called the argument of the elliptic function and $0 \leq k \leq 1$ is referred to as the modulus.

Elliptic Integral of the Third Kind: $\Pi(\varphi, \alpha^2, k)$

We note that there is a third kind of normal elliptic integral given by

$$\Pi(\varphi, \alpha^2, k) = \int_0^\varphi \frac{d\vartheta}{(1 - \alpha^2 \sin^2 \vartheta) \sqrt{1 - k^2 \sin^2 \vartheta}},$$

where $-\infty < \alpha^2 < \infty$ is another parameter.

Please note that we have included the definition for the elliptic integral of the third kind for completeness although it is not otherwise referred to in the remainder of this course and neither will it form part of the exam.

Complete Elliptic Integrals

When $\varphi = \pi/2$ then the elliptic function is said to be **complete** and the argument is usually dropped. The notation we will use is

$$K(k) = F(\pi/2, k), \quad E(k) = E(\pi/2, k),$$

where we note that (for historical reasons) only in the case of the elliptic function of the first kind is the letter denoting the function changed for the complete case.

We also define the complimentary modulus k' which is given in terms of the usual module by

$$k' = \sqrt{1 - k^2}.$$

Legendre's relation

The complete elliptic integrals of the first and second kind are related by the expression

$$E(k)K(k') + E(k')K(k) - K(k)K(k') = \pi/2,$$

which is called Legendre's relation.

The elliptic integrals also reduce to greatly simplified expressions for particular value of the argument and modulus. Some of these are

$$F(0, k) = E(0, k) = 0,$$

$$F(\varphi, 0) = E(\varphi, 0) = \varphi,$$

$$F(\varphi, 1) = \sin \varphi,$$

$$E(\varphi, 1) = \log(\tan \varphi + \sec \varphi).$$

Interaction energy between molecules

For two separate molecular structures (or non-bonded), the interaction energy E can be evaluated using either a discrete atom-atom formulation or by a continuous approach.

Discrete Method

The non-bonded interaction energy may be obtained as a summation of the interaction energy between each atom pair, namely

$$E = \sum_i \sum_j \Phi(\rho_{ij}),$$

where $\Phi(\rho_{ij})$ is the potential function for atoms i and j located a distance ρ_{ij} apart on two distinct molecular structures, and it is assumed that each atom on the two molecules has a well defined coordinate position.

Continuum approach

The continuum approximation assumes that the atoms are uniformly distributed over the entire surface of the molecule, and the double summation on the previous slide is replaced by a double integral over the surface of each molecule, thus

$$E = \eta_1 \eta_2 \int_{\mathcal{S}_2} \int_{\mathcal{S}_1} \Phi(\rho) dA_1 dA_2,$$

where η_1 and η_2 represent the mean surface density of atoms on the two interacting molecules, and ρ represents the distance between the two typical surface elements dA_1 and dA_2 located on the two interacting molecules.

Mean atomic surface density

The mean atomic surface density η is determined by dividing the number of atoms which make up the molecule by the surface area of that molecule. The following table outlines the surface density of carbon atoms on various carbon nanostructures which are examined in this course. The continuum approximation is rather like taking the average or mean behaviour.

Structure	η (atoms·Å ⁻²)
Graphene	0.3812
Carbon nanotube	0.3812
C ₆₀ fullerene	0.3789
C ₂₄₀ fullerene	0.3767
C ₅₄₀ fullerene	0.3898

Example 1

Determine the surface density of carbon atoms on a sheet of graphene or a carbon nanotube.

A graphene sheet consists of a tessellation of hexagonal rings, so that each atom contributes one third to the total number of atoms in the ring since each atom is also bonded to two other hexagonal rings. Since there are six carbon atoms per hexagon

$$\eta = (1/3 \times 6)/A_{hex} = 2/A_{hex},$$

where A_{hex} is the surface area of one hexagonal ring.

Example 1 solution

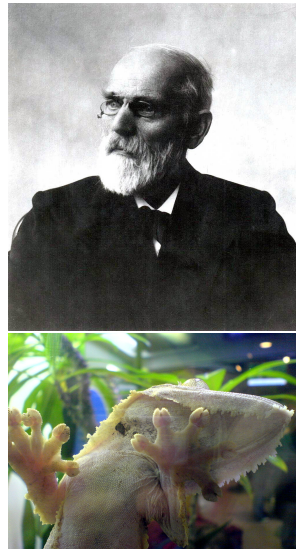
The surface area of one hexagon ring is $A_{hex} = 3\sqrt{3}\sigma^2/2$, so that the surface density of carbon atoms becomes

$$\eta = 4/(3\sqrt{3}\sigma^2),$$

where the units of the atomic surface density are $\text{atoms}\cdot\text{\AA}^{-2}$, and for a sheet of graphene with $\sigma = 1.421 \text{ \AA}$ the atomic surface density is $\eta = 0.3812 \text{ atoms}\cdot\text{\AA}^{-2}$.

Interaction forces

The **van der Waals force** refers to the attractive or repulsive force between molecules, or the intermolecular force. It is named after the Dutch scientist Johannes Diderik van der Waals (1837-1923) since he was one of the first to propose an intermolecular force. For his work on the equation of state for gases and liquids he won the 1910 Nobel Prize in Physics. The van der Waals force is visible in nature, for example the gecko climbs walls with use of the van der Waals force between the wall and the gecko's setae, or hair-like structures, on their feet.



Interaction forces

The van der Waals interaction force between two typical non-bonded atoms of two molecules is given by

$$\mathbf{F}_{vdW} = -\nabla E,$$

where the energy E is given by either the discrete or continuum approach, and the symbol ∇ refers to the vector gradient operator. In Cartesian coordinates the gradient operator is given by

$$\nabla = \mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z},$$

where \mathbf{i} , \mathbf{j} and \mathbf{k} , denote unit vectors in the x -, y - and z -directions, respectively.

Interaction forces

So for example, if we have a geometry which is rotationally symmetric around the z -axis then the resultant force in the axial direction (z -direction) is obtained by differentiating the total interaction energy E , calculated from either the discrete or the continuum approach, with respect to z , therefore the van der Waals force \mathbf{F}_{vdW} simplifies to become a force purely in the z -direction, given by

$$\mathbf{F}_{vdW} = kF_z,$$

where

$$F_z = -\frac{\partial E}{\partial z},$$

since by symmetry the forces in the other directions are in balance (net equal to zero).

Lennard-Jones potential

Sir John Lennard-Jones (1894-1954), a mathematician knighted in 1946, is regarded as the father of modern computational chemistry due to his contributions in theoretical chemistry. In particular, Sir Lennard-Jones had interests in quantum mechanics and intermolecular forces. The interests led to his most notable contribution, the atomic interaction potential proposed in 1924, and which now bears his name.



Lennard-Jones potential

The Lennard-Jones potential describes the interaction between two non-bonded atoms and is given by

$$\Phi(\rho) = -A\rho^{-m} + B\rho^{-n},$$

where A and B are referred to as the attractive and repulsive constants, respectively, and ρ is the distance between the atoms.

In many cases the values $m = 6$ and $n = 12$ are adopted, and this is commonly referred to as the 6-12 potential. For hydrogen bonding interactions a 10-12 potential is used and it should be noted that there are a number of other empirically motivated potentials in the literature, such as the Morse potential.