

Exploring Fourier Transform Techniques with Mathcad

Mark Iannone
Department of Chemistry
Millersville University, Millersville, PA 17551

Fourier transform instruments are common in the modern laboratory. While an understanding of the Fourier transform is not necessary to operate an FT instrument or to understand its advantages, it is useful to have at least a pictorial notion of how it works, since "FFT concepts tend to remain an abstraction not easily grasped and certainly readily forgotten." [1] A graphical approach is suggested here. The four Mathcad¹ documents in the accompanying collection carry out Fourier transforms on fabricated data sets and graph both the original and the transformed data. The resulting graphs are familiar ones [2]; however, unlike a printed page, a Mathcad document can be experimented with in order to obtain a feel for the relationship of data to its transform.

The four Mathcad documents are structured similarly; variables and parameters are named in corresponding ways in each of the documents. Here, the focus is on the data, and the related laboratory instruments are not discussed. Detailed descriptions of instruments are readily available, of course, and references are suggested below.

Introduction

Fourier analysis

Functions satisfying the Dirichlet conditions (one of which is periodicity) can be written as a sum of a series of sines and cosines, called a Fourier series. For example, the sum

$$f(t) = \sum n^{-1} \sin[n(2\pi vt)], \quad 1.$$

$n = 1, 3, 5, \dots$, approximates a square wave. In the reverse of this process, given a waveform, one can determine its frequency makeup by Fourier analysis.

The Fourier transform

The Fourier transform relates a function to another function of a conjugate variable. In chemistry, the most common conjugate pairs are time/frequency, which occurs in short-pulse experiments such as ultrafast laser spectroscopy and FTNMR; and length/wavenumber, which occurs in FTIR.

Fourier transformations of some functions can be carried out analytically, but in the case of experimental data this is not possible. The discrete Fourier transform does not transform the continuous function; it takes a number of evenly spaced points that sample the function and produces a sample of the transform. The fast Fourier transform (FFT), an algorithm "brought to the attention of the scientific community by Cooley and Tukey," [3] takes advantage of redundancy in the process of calculating a discrete FT; for example, in the case of 2^k data points the calculation is shortened by a factor of roughly $2^{k+1}/k$. [3, 4] This algorithm and computer hardware implementing it have made FT instruments practical.

Discrete data imposes limitations, however. Suppose samples are taken at time intervals τ for a total sampling time of A . Then the highest frequency that can be unambiguously identified in the FT, the Nyquist frequency, is $(2\tau)^{-1}$. The resolution of the spectrum (i.e. the FT) will be at best A^{-1} . These important factors are explored in the accompanying documents.

¹ Mathcad is a registered trademark of MathSoft, Inc.

Mathcad documents

Four Mathcad documents have been developed to illustrate different aspects of the Fourier transform. No prior familiarity with Mathcad is required to work through them. However, some of the exercises require the student to edit and format equations and graphs. If the remarks contained in the documents do not provide sufficient guidance, the Help file or the manual can be consulted.

The documents have the following structure in common. m is the number of data points in the data set or array ("vector" in Mathcad parlance) to be transformed; $m = 2^k$. (The number of elements in the vector must be a power of two in order to use FFT, although the CFFT function does not have this restriction.) The sampling interval is τ for time/frequency and λ for the IR simulation. The vector \mathbf{y} holds fake experimental data. Along with a second variable t or x , there is a set of m pairs (t_i, y_i) , time vs. intensity; or (x_i, y_i) , length vs. intensity. The transform of \mathbf{y} produces a vector \mathbf{Y} with half as many elements, yielding a set of data pairs of frequency vs. intensity, (f_j, Y_j) ; or wavenumber vs. intensity, (w_j, Y_j) .

Best use can be made of the documents by experimenting with the parameters. As a guide, many numbered exercises are included, which could be used as the basis for a written assignment. Please note that best results will be obtained when the Automatic Computation option in the Math menu is NOT checked.

FT1Intro.mcd: Fourier analysis of a waveform

This introductory document illustrates in detail how sampling gives rise to the Nyquist frequency and aliasing. The limits of spectral resolution are also explored. In order to illustrate the speed advantage of the FFT, an integral transform is done.

The waveform in this document has two frequency components. The vector \mathbf{y} is a set of samples of the amplitude, evenly spaced in time. The vector \mathbf{Y} is the Fourier transform of \mathbf{y} ; it shows the frequency makeup of the waveform. The frequency corresponding to the j th element of \mathbf{Y} is j/t_{m-1} where t_{m-1} is the sampling time.

FT2IR.mcd: Fourier transform of an interferogram

In an interferometer, a beam of light is split into two beams, each with half the original intensity. These two beams travel paths whose lengths differ by x before recombining to form one beam again. The electromagnetic fields due to light of wavelength λ present in the beam will interfere constructively when $x = n\lambda$, n an integer, and destructively when $x = (n+1/2)\lambda$. Looked at the other way around, light of a given wavelength will contribute to the recombined beam for some values of x but not for others. Thus the graph of intensity of the recombined beam vs. the path-length difference x , called an interferogram, contains information about the frequencies present in the beam. In fact, the Fourier transform of the interferogram is a partial frequency spectrum of the light source.

If the light passes through an absorber, its frequency content is changed, and this information is contained in the interferogram and its Fourier transform. This is the principle of the FTIR.[5,6] Three advantages of this method of acquiring the spectrum are (1) throughput: low light loss due to simple optical system; (2) multiplex: the whole spectrum of the source arrives at the detector; and (3) high wavenumber accuracy. [7,8,9]

In this Mathcad document, the inverse FT is used to generate an interferogram from a spectrum: a simulated black body (no CO₂ or water added!) with two notches representing absorption. The sampling interval, 6.328×10^{-5} cm, is the wavelength of the HeNe laser used to monitor interferometer movement, and cannot be altered on a standard instrument. The only

accessible experimental parameter is the distance traveled by the interferometer mirror, which is proportional to m in this document. The relationship of this to the resolution is investigated in some of the questions within the document.

The intensity of light of wavenumber w at interferometer position x is given by [10]

$$y(x, w) = Y(w)[1 + \cos(2\pi wx)] \quad 2.$$

in which $Y(w)$ is the spectral intensity at w . The total intensity at position x is the integral over the spectrum:

$$y(x) = \int_0^{\infty} Y(w)[1 + \cos(2\pi wx)] dw \quad 3.$$

The first term is a constant while the second is the Fourier transform of the spectrum:

$$\begin{aligned} \int_0^{\infty} \cos(2\pi wx) dw &= \int_0^{\infty} \frac{e^{2\pi iwx} + e^{-2\pi iwx}}{2} dw \\ &= \frac{1}{2} \int_{-\infty}^{\infty} Y(w) e^{2\pi iwx} dw. \end{aligned} \quad 4.$$

The skeptic will object that using IFFT followed by FFT is circular reasoning. However, direct calculation of the interferogram using Equation 3 is tractable only if $Y(w)$ is very simple, and Equation 4 shows that the two procedures are equivalent.

FT3Pulse.mcd: Fourier transform of a pulse

A continuous source of radiation (a continuous-wave laser, for example) can be highly monochromatic, that is, have a narrow frequency distribution. A short sample of a wave (a laser pulse, for example) must contain a range of frequencies. The relationship between spectral bandwidth and pulse duration is given approximately by [11]

$$\Delta\nu\Delta t > 0.5. \quad 5.$$

This is illustrated in the Mathcad document by comparing the transform of a long section of a monochromatic sine wave with that of a short section of the same wave. The fundamental frequency is set as 100 Hz and the total sampling time A is set at 0.5 s. The default pulse is square, but the important case of a Gaussian pulse is investigated in Exercises 3.6 and 3.7.

FT4Free Ind Decay.mcd: Fourier transform of a free induction decay

FTNMR has been compared to evaluating a bell by striking it and analyzing the resulting ringing. [12,13] A short RF pulse is the blow while a transient oscillating magnetic moment is the ringing. The fundamental frequency of the pulse is near the Larmor frequency of the nucleus; as demonstrated before, a pulse must contain a range of frequencies. The pulse is short enough that all nuclei of interest (with slightly different Larmor frequencies due to different chemical environments) are irradiated equally. [14] The oscillating magnetic moment is detected by the NMR's receiver; each affected nucleus contributes a frequency to the oscillation. Like a bell's ringing, the signal dies away with a characteristic decay time T_2^* . [15] This free induction decay (FID) is referenced to the fundamental frequency and recorded, then Fourier-transformed to obtain the frequency spectrum (i.e. the NMR spectrum) of the sample, in which a peak appears for each nuclear frequency present in the FID. Typical proton T_2^* times in liquid samples are on the order of 10 s. [16] The full range of the NMR spectrum is around 10 ppm (e.g. 100,000,000 to

100,001,000 Hz for a 100 MHz NMR), so the frequency *difference* between fundamental and FID signal is digitized. Complete descriptions of the pulsed NMR experiment may be consulted for details. [12-18]

The Mathcad file contains an artificial FID with 3 frequencies having 3 different decay times, which is then transformed. Many NMR peaks are extremely narrow, corresponding to long T_2^* times. However, in this demonstration the T_2^* times are made short enough that their effect can be appreciated.

Acknowledgment

The author wishes to thank Prof. Theresa Julia Zielinski for detailed suggestions which greatly improved the presentation of the Mathcad documents, and Dr. John S. Phillips for stimulating discussion, valuable suggestions and help with the literature search. The manuscript benefited greatly from the thoughtful comments of three reviewers as well.

Literature Cited

1. C. Steel, T. Joy, T. Clune; "Teaching FFT Principles in the Physical Chemistry Laboratory;" *J. Chem. Educ.*; 67(10); 883-887, 1990.
2. Glasser, L.; "Fourier Transforms for Chemists, Part II. Fourier Transforms in Chemistry and Spectroscopy;" *J. Chem. Educ.*; 64(11), A260-A266, 1987.
3. Arfken, G; *Mathematical Methods for Physicists*; Academic Press: Orlando, 1985; p. 791.
4. Bergland, G. D.; "A guided tour of the fast Fourier transform;" *IEEE Spectrum*; July, 1969; 41-52.
5. Griffiths, P. R. ; deHaseth, J. A.; *Fourier Transform Infrared Spectroscopy*; Wiley-Interscience: New York, 1986.
6. W. D. Perkins, "Fourier Transform Infrared Spectroscopy, Part I. Instrumentation;" *J. Chem. Educ.*; 63(1), A5-A10, 1986.
7. Skoog, D.A.; Leary, J.J.; *Principles of Instrumental Analysis*; Saunders College Publishers: Ft. Worth, 1992; Chapters 6, 12.
8. Griffiths, P. R.; "Fourier Transform Infrared Spectroscopy," *Science*; 222; 297-301, 1983
9. W. D. Perkins; "Fourier Transform Infrared Spectroscopy, Part II. Advantages of FT-IR;" *J. Chem. Educ.*; 64(11), A269-A271, 1987.
10. Fowles, G. R.; *Introduction to Modern Optics*, Dover Publications: New York, 1989; p. 80
11. Fleming, G.; *Chemical Applications of Ultrafast Spectroscopy*; Oxford University Press: New York, 1986.
12. Atkins, P. W.; *Physical Chemistry*; W. H. Freeman: New York, 1994; Chapter 18
13. Derome, Andrew; *Modern NMR Techniques for Chemical Research*; Pergamon Press: Oxford, 1987; Chapter 2
14. Friebolin, H.; *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Publishers: Weinheim, 1993; Chapter 1
15. Fukushima, E. and Roeder, S. B. W.; *Experimental Pulse NMR: A Nuts and Bolts Approach*; Addison-Wesley Publishing Co.: Reading, 1981 ; Section I.C.1.
- 16 Ref. 14, p. 178
17. King, R. W.; Williams, K. R.; "The Fourier Transform in Chemistry, Part 1. Nuclear Magnetic Resonance: Introduction;" *J. Chem. Educ.*, 66(9), A213-A219, 1989
18. King, R. W.; Williams, K. R.; "The Fourier Transform in Chemistry, Part 2. Nuclear Magnetic Resonance: The Single Pulse Experiment;" *J. Chem. Educ.*, 66(10), A243-A248, 1989